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SHAW'S MANUAL OF ELECTRO-METALLURGY.

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Unavoidable circumstances having prevented the revision of the Proof Sheets by the Author, the following errors have occurred, which the reader will please correct :—

Index, for "Platiman," read "Platinum"
Page 6, line 30, for "oxide of potassium," read "iodide of potassium"
„ 10, line 32, for "Farraday," read "Faraday"
„ 14, line 3, for "beat," read "bent"
„ 15, line 24, for "extra," read "extreme"
„ 15, line 12 in note, for "ammoniate," read "ammonia"
„ 15, lines 14 and 15 in note, for "saturative," read "saturated"
„ 16, line 3, after "negative," insert "plate"
„ 23, line 16, for "deposit, the fac simile," read "deposit ;—the fac simile"
„ 24, line 15, for "pur," read "press"
„ 37, line 17, for "adapted to," read "adopted for"
„ 39, line 44, for "form," read "forms"
„ 40, line 10, for "superfluities," read "superfluity"
„ 45, line 30, for "experiments," read "experimenters"
„ 45, line 35, for "produced," read "precipitated"
„ 46, line 10, for "cyanagen," read "cyanogen"
„ 46, line 32, after "ammonia," insert "and"

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A MANUAL

OF

ELECTRO-METALLURGY.

BY

GEORGE SHAW.

LONDON:
R. GROOMBRIDGE, PANYER ALLEY, NEWGATE STREET.

MDCCCXLII.

Entered at Stationers' Hall.

BIRMINGHAM:
ALFRED ALLEN, PRINTER TO THE QUEEN,
3, COLMORE ROW.

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PREFACE.

THE following pages contain the principal facts of the Art of Electro-Metallurgy.

The author has endeavoured to introduce everything interesting to the experimenter in this novel art; but has at the same time sought to make the work as brief as possible, by the omission of some of the minute details of manipulation. To the beginner this may appear discouraging, but in the end he will find it to his advantage; for although by giving minute directions in the manipulatory processes, a person wholly unacquainted with the principles on which those processes are founded may *possibly* succeed in his experiments, yet the *probability* is that he would fail in the majority of cases, and would find himself compelled to master the principles of the science of Voltaic Electricity, before he could proceed to his experiments with the certainty of success.

The author would not be understood to mean that the subject of manipulation has been neglected; on the contrary, he has endeavoured to introduce all that is essential; and he believes that a careful perusal of the following pages, combined with that knowledge, which experiment *alone* can give, will enable any one to practice the Art of Electro-Metallurgy, as far as it is at present developed.

As the facts stated in this work (with a few trifling exceptions,) have been experimentally verified by the author, he feels little doubt of their general accuracy.

Temple Row, West, Birmingham,
May 16th, 1842.

INDEX.

Page

Acid, battery 32
Action of the Voltaic Battery explained 5
Affinity of oxygen for copper at the positive electrode 21
Adhesion prevented 23
Air bubbles, to be avoided in moulds 30
Amalgamated zinc, experiment with 4
Amalgamation, how effected . . . . . NOTE 4
Anode defined 10
Application of the Voltaic Battery to etching 41

Battery, acid 32
——— Babbington's 3
——— Cruikshank's 4
——— De Moleyn's . . . . . NOTE 15
——— Daniell's 12
——— Grove's 14
——— Smee's 15
——— Wollaston's 3
——— best kinds for electro-metallurgical operations 32
——— directions for charging acid 32
——— ditto ditto Daniell's 32
——— effect if too large 34
——— ditto small 34
——— action of, how regulated 32
——— quantity explained 7
——— intensity explained 9
Black-lead a conductor 27
——— preparation of surfaces with 27
——— used for bronzing 37
Brittle copper, causes which produce 34, 35
——— how avoided 34
Bronzing, various methods of 37

Chemical effects of the Voltaic Battery 10
Constant battery 12
Copper, produced of various qualities 35
——— plates, multiplied by the Electrotype 37
Courronne des tasses. 3
Cyanide of gold, decomposition of 45
——— potassium, preparation of 46
——— silver, decomposition of 46

Daguerréotype plates, nature of 43
——— copied 43
Daniell's battery 12
Decomposition, voltaic 11
——— cell introduced 20
——— of acetate of copper 36
——— of nitrate of copper 36
——— of salts of gold 45
——— of ditto platinum 45
——— of ditto silver 45
Diaphragms of animal membrane 17
——— plaster of Paris 17
——— wood 17

Page

Electrotint, Palmer's 38
Electroype, copying of medals, &c. by 17
———— history of 16
———— improvements in 19

Fusible metal, composition of 24
———— how used for making moulds 24

Gold, decomposition of the salts of 48

Heat, effect of, on the battery, &c. 36
Hydrogen, released at the negative surfaces of the battery 8
———— reduction of metals by nascent 11

Introduction 1
Iodide of potassium, decomposed by a feeble current 6
Iron, deposition of copper upon 37

Medals, copying of 17
Moulds, making of 28
——— fusible metal 24
——— lead 24
——— wax 25
Muriate of Ammonia, use of in batteries . . . . 15 NOTE 19

Oxygen, combines with bodies at positive electrode 21
——— developed at positive electrode 21
Oxide of silver, preparation of 46

——— of gold, do. do. 45
Plaster casts, making of 25
———— prepared 27
Platinode, defiition of 10
Platiman, reduction of 47
Plumbago, use of 27
———— differcnce in various samples 28
Poles of a battery 10

Salts, decomposition of by battery 11
Secondary effects of battery 11
Series of decomposition cells 22
Silver, reduction of 45, 48
Single cell apparatus, various forms of 19
Smee's battery 15
Solids, not decomposed by the battery 10
Spencer's experiments 16

Table of experiments on reduction of copper 35
Temperature, effects of 36

Volta's pile 2
Voltaic batteries, their respective advantages 15

Zinc, experiments with amalgamated 4
———————— impure 4
———————— pure 4
Zincode explained 10

A MANUAL

OF

ELECTRO-METALLURGY.

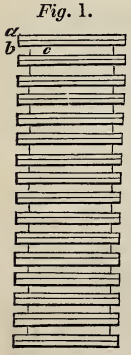
In reviewing the early history of the physical sciences, we cannot but be struck with the fact, that many discoveries, which now, either minister to our wants, or add to the number of our enjoyments, lay for a long time after their announcement wholly neglected, or at best, served but to swell the pages of the historian. It is not so, however, in modern times: no sooner is a discovery now made, than its application to some useful purpose is attempted; and at this moment, there are probably hundreds anxiously watching the progress of discovery, eager for the announcement of some fact which may be made available to purposes of use or ornament. There is no department of science more illustrative of these remarks, than that branch of the science of Electricity, which the following pages are intended to illustrate—namely, the Precipitation of Metals by Voltaic Agency. During the short period that has elapsed since the constant battery of Professor Daniell was made public, a fact which was pointed out by the action of that instrument, has given rise to a new application of the voltaic battery, which has already worked the most important changes in the production of works of art. In treating of the voltaic battery, we shall fully describe the invention of Professor Daniell. It will suffice to notice in this place the fact, that the solution of sulphate of copper used in the excitation of that instrument, suffers rapid decomposition, and that the metallic copper which is precipitated attaches itself closely to the copper cylinder in which the solution is contained; and it was found, on detaching the precipitated metal, that it had been deposited in such intimate contact with the copper cylinder, that the most minute marks thereon had been faithfully copied. The application of this fact constitutes the art of Electrotype.

From this it would appear that the history of the art is so simple as to require no comment, and so modern as to admit of no dispute: such, however, is not the case. It is a subject which has given rise to the most

angry discussions; and concerning which, even now, opinion is strangely divided. In these disputes we shall not take part, but shall proceed at once to describe the origin and progressive improvement of that instrument, so intimately connected with the progress of the science of voltaic electricity—namely, the galvanic or voltaic battery; and with the facts of the science before him, we doubt not that the reader will form a just appreciation of the labours of those, who, by the application of these facts, have originated the art in question; and, as a knowledge of the principles of voltaic electricity is essential to its successful practice, we shall take occasion to treat of those principles, while tracing the history of the voltaic battery.

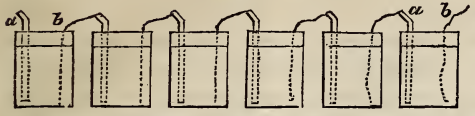
The science of Voltaic Electricity originated in an experiment made by Galvani in the year 1790. He observed that, on placing a recently killed animal upon a plate of zinc, and touching it with a wire or plate of copper, also in contact with the zinc, violent contractions of the muscles of the animal immediately occurred. Though it was this experiment that determined the masterly researches of Volta, and from which the science must date its origin; yet an analagous fact was known long prior to Galvani's discovery. It had been announced in an obscure German work, entitled "The General Theory of Pleasures," that if a plate of zinc were placed upon the tongue, and a piece of silver under it, a strange taste would be observed each time the edges of the pieces of metal were brought in contact. This experiment, however, attracted no attention, and cannot be said to have any connection with the progress of our science. In repeating the experiments of Galvani, Volta was led to the construction of an instrument, which, in honour of its illustrious inventor, is called the voltaic pile. This instrument consists of a series of plates of dissimilar metals, usually copper and zinc; these, to the extent of forty or fifty, are piled upon each other in regular succession, a piece of card or flannel, wetted with a saline or acid solution, being interposed between the metals of each pair. It is represented in *fig.* 1, where *a* is the plate of zinc, *b* the plate of copper, and *c* the moistened flannel. It was found that the effects of this instrument were much more powerful than those of a single pair of plates, and that it exhibited a series of new and extraordinary phenomena. If the moistened hands were brought in contact with the ends of such a pile, a distinct shock would be felt; and the leaves of gold-leaf electrometers similarly situated were observed to diverge. By connecting wires to the ends of this instrument, and plunging them in water, minute bubbles of gaseous matter will escape from them: on examination, these bubbles will be found to consist of oxygen and hydrogen, the gaseous constituents of water. The wires thus connected to the ends of the pile were called its poles, and by them the effects of the instrument could be transmitted to almost any distance. This arrangement of the elements

Fig. 1.



was, however, in many respects inconvenient; and Volta contrived another arrangement, which he called the *couronne des tasses*—(see *fig.* 2). This instrument consisted of any number of vessels containing the acid solution, and an equal number of bars of zinc *a* and silver *b* soldered end to end, and so bent that, while the zinc bar rests in one of the vessels, the slip of silver soldered to it hangs in the other. This arrangement is decidedly superior to the pile; and it is worthy of remark, that the voltaic batteries of the present day scarcely differ from this modification.

Fig. 2.



The next alteration in the voltaic apparatus was made by Mr. Cruikshanks—(*fig.* 3). The plates in his battery were square, and the copper *a* and zinc *b* of each pair were soldered together. These compound plates were cemented in grooves cut transversely in a wooden trough, and they themselves, formed a series of compartments for holding the exciting liquid. In using this instrument, the dilute sulphuric acid was poured into the trough, which was so inclined that each compartment became filled with an equal quantity of the liquid. This instrument possesses many inconveniences: if the plates are situated at a great distance from each other, the action is impeded; and if, to remove this objection, the plates are placed near to each other, the cells are too diminutive to hold the requisite quantity of acid. The impossibility of removing the zinc plates for the purpose of cleaning them, is also a serious objection. These inconveniences suggested the modification called Babbington's battery—(*fig.* 4). This consists of an earthenware trough, divided into a number of compartments, in each of which is placed a plate of zinc *a*, and near to that a plate of copper *b*, the zinc of one cell being connected with the copper of the next. The series is suspended from a bar of wood. This battery, like the former, is excited by dilute sulphuric acid: its superiority consists in the facilities afforded for removing the zinc plates, and in the close approximation of the metals—a point of great importance. It was by an instrument of this kind that the splendid experiments of Davy were performed.

Fig. 3.

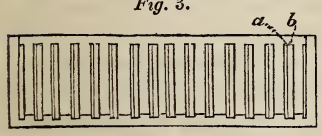
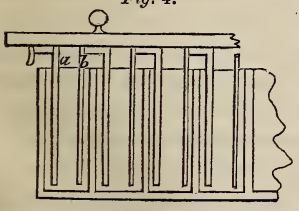


Fig. 4.



The next improvement was introduced by Dr. Wollaston. He completely surrounded the zinc with the copper,—an alteration which was found to increase the amount of available power to nearly double that, previously obtained from an equal extent of zinc surface. The improvement which comes next in order is, perhaps, the most important one that has yet been introduced; it is the amalgamation of the surfaces of the zinc plates by

mercury.* For this valuable contribution we are indebted to Mr. Kemp. In order to render the importance of this improvement obvious, it will be necessary to resort to experiment.

If a plate of ordinary zinc be plunged in dilute sulphuric acid, violent effervescence occurs; the oxygen of the water (as will presently be shown) combines with the metal, forming oxide of zinc, which uniting with the sulphuric acid forms sulphate of that metal; while the hydrogen, the other element of the water, escaping in the gaseous form, occasions the effervescence observed; eventually, the zinc disappears, and the dilute acid is replaced by a solution of the sulphate of that metal. If during the time this phenomenon is taking place a strip of copper be introduced into the solution, and made to touch the zinc, effervescence also occurs at its surface, by the escape of hydrogen, although it will be found that no chemical action takes places upon the copper. The escape of hydrogen, however, will be much less than at the surface of the zinc. Now, inasmuch as the copper has not been chemically acted on, it is evident that the hydrogen appearing at its surface can only result from the decomposition of the water effected by the zinc, and its appearance in such a part of the arrangement is at first sight calculated to excite surprise. This circumstance becomes, however, satisfactorily explained, when we find that pure zinc is perfectly insoluble in dilute sulphuric acid, excepting in contact with another metal; and then, although the whole of the chemical action takes place at the surface of the zinc, the whole of the hydrogen escapes at the surface of the metal in contact with it. We shall not enquire in this place *why* the hydrogen appears in such a part of the arrangement; it is sufficient that we know the fact, as it enables us to understand the experiment under consideration. We now perceive, in relation to that experiment, that in reality not an atom of hydrogen presents itself at the true surface of the zinc, but that is evolved from the particles of foreign metals and charcoal with which the zinc is contaminated, and which are scattered about its surface. In other words, that which takes place on the large scale, when a plate of pure zinc is associated with a plate of copper, and immersed in the acid solution, takes places on a small scale when impure or ordinary zinc is used alone, the surface of that metal presenting almost an infinity of such combinations. We shall presently show that the only available action in the voltaic battery is that by which the hydrogen is delivered at the surface of the copper plate, and that, consequently, an immense expenditure of materials is occasioned by that local action in ordinary zinc, of which we have spoken—an action which we can neither suspend, nor in the slightest degree control. By using pure zinc, however, the whole of the chemical action is turned to account; not a particle of zinc is dissolved, but it renders up in an

* Zinc is very easily amalgamated. It is only necessary to immerse it for a few moments in dilute sulphuric acid, in order to clean its surface. If it now be plunged into mercury, it will be found on removing it, that it has acquired a perfect coating of that metal; or the mercury may be poured on the zinc, and spread about by a rag or hare's foot—a more economical and equally effective plan.

available form that amount of voltaic electricity which is necessarily associated with such solution, but which, as already explained, with the ordinary metal, is evolved under circumstances which render it useless. The use of pure zinc in the construction of voltaic batteries would be attended with such expense, that, that alone, is sufficient to prevent its introduction; indeed the improvement in the voltaic battery now under consideration (the amalgamation of the zinc) renders its use unnecessary.

Many experiments had been made by Sir H. Davy and others on amalgamated zinc, but for its introduction into the voltaic battery we are indebted to Mr. Kemp. Zinc, the surface of which is amalgamated or covered with quicksilver, is, like pure zinc, insoluble in dilute sulphuric acid, unless in contact with another metal; in short, plates of amalgamated zinc conduct themselves in every respect like plates of pure zinc; and what has been said of the pure metal applies to that which is impure, when its surface is amalgamated. Many explanations have been given of the action of the mercury; but as most of these are more or less unsatisfactory, we shall not enumerate them, but content ourselves with a knowledge of the fact.

Other very important improvements have been made in the voltaic battery by Daniell, Grove, and Smee. We shall defer the consideration of these for the present; for—as we have hitherto said nothing in explanation of the cause of the phenomena of the battery, and as we have arrived at that point in its history where those phenomena are definite and controllable; and as we are, further, in the midst of experiments which are well suited to illustrate the action of this remarkable instrument—we shall avail ourselves of the present, as the most favourable opportunity, for attempting that explanation.

The reader will bear in mind what has been said of the plates of amalgamated zinc and copper introduced into sulphuric acid,—namely, that action only takes place during the time that the metals are connected together (either immediately, or by the intervention of a third piece of metal); that, if they are removed from each other, however small the distance, the evolution of gas ceases. If the plates are allowed to remain in contact, after a considerable time (dependent on the proportions of the ingredients) the effervescence will become less violent, and eventually will cease. Let us now proceed to analyze the experiment: the zinc weighs considerably less than when introduced; the sulphuric acid is replaced by a solution of the sulphate of zinc; the copper is wholly unaffected; and the gas evolved from the latter metal is found to be hydrogen. An attentive consideration of these results leads us to the conclusion, that the water of the dilute acid has been decomposed; for, as the sulphate of zinc produced is a compound of sulphuric acid and the oxide of zinc, it is evident that oxygen must have been supplied to that metal by the water; and this view is confirmed by the fact, that the hydrogen given off by the copper is in such proportion, that, if combined with the oxygen of the

oxide of zinc, water would be the product. In this experiment the enquiry arises,—Why do not the oxidation and solution of the zinc take place without the presence of a second metal, and how comes it, that the hydrogen resulting from the decomposition of the water does not present itself at the surface of the zinc, where it is developed, but passes through the liquid, and is evolved at the other metal? The question suggests the answer:—the facts, that the metals must be in intimate contact, and both immersed in the same acid,—that the only element set free is carried to a point, at a considerable distance from that at which it is liberated,—demonstrate that the chemical action which takes place is accompanied by the circulation of some extraordinary power, or would seem rather to be dependent on it; for when, by breaking the contact between the plates, we interrupt its circulation, all chemical action ceases.

That some new power is thus called into action, we have abundant evidence. It has already been observed that the plates, instead of being in actual contact, may be connected together by a third piece of metal; nay, if a stout copper wire, a mile long, be employed, and one end of it be touched against the zinc, and the other against the copper, the same phenomena will be presented. Now, the whole length of this connecting wire exhibits some remarkable changes in its physical characters. Before its introduction between the plates of our rude voltaic apparatus, it was perfectly inert with regard to magnetic bodies; but now it attracts iron filings as though it were a magnet; and a compass needle brought near to it is powerfully deflected. It exhibits, moreover, calorific and chemical phenomena. By making the connection between the plates with a short and very fine wire, a powerful calorific effect will be developed; the wire will glow with the most intense heat; and if the action of the apparatus be sufficiently energetic, will be fused and dissipated in minute globules, or will burn with a brilliant scintillation. Again, let the connection between the plates be made through the solution of some chemical compound, easily decomposed—oxide of potassium for example—and the elements of that compound will be separated. All these facts demonstrate the operation of some subtle power, which, from its presence in every part of the arrangement, is believed to circulate through it, and, under the circumstances enumerated, to develope itself in the various forms of magnetism, heat, and light.

This agent is called by the names of galvanism, voltaic and galvanic electricity. Of its ultimate nature, as of that of every other natural agent, we know literally nothing; nor does our knowledge of its effects enable us even to frame a consistent theory. By some philosophers it is considered as a fluid subtle in the highest degree,—pervading every species of matter,—unrecognised when quiescent, and developing itself in the various forms before spoken of, when, by the arrangement of the necessary conditions, it is set into circulation. Others, again, have been led by its effects to consider it as a compound fluid, which only puts forth its extraordinary powers when decomposed; that this decomposition takes place in the voltaic battery; and

that these fluids are circulating through that apparatus in contrary directions. Other philosophers have rejected the idea of circulation: they regard it as an affection of ordinary matter, or of the hypothetical ether, whose vibrations constitute light. Nor are these the only theories that have been framed to connect together the beautiful phenomena of electricity: scarcely a philosopher of distinction can be pointed out who does not entertain views on this subject peculiar to himself. We shall not follow these speculations into detail, but content ourselves with a knowledge of the facts of the science.

The reader will have remarked that the apparatus just now described differs from the pile of Volta and the other batteries which have been enumerated, inasmuch as it consists of but one pair of plates, while they are formed by the assemblage of several such pairs. The pile or battery is a series of arrangements similar to the one just experimented with, so disposed that the zinc of one cell is connected with the copper of the next, the zinc of that with the copper of a third, and so on, to any extent. Such a form of instrument is called an intensity arrangement, while the single pair of plates is called a quantity arrangement—properties which we will now illustrate.

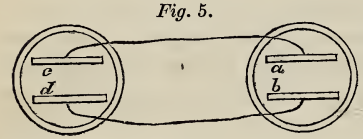
A single voltaic pair, it has already been said, will decompose iodide of potassium; but if the connection between the plates be made with other compounds, water for example, no decomposition of the water will take place; the voltaic current will not pass (for water can only conduct it by suffering decomposition) and, consequently, the battery will be as inactive as though no such connection had been made. If, however, water be made the medium of communication between the ends of a compound battery consisting of nine or ten pairs, the water will be rapidly decomposed, and the voltaic current will pass, as the escape of hydrogen at the surface of each copper plate of the battery will demonstrate. The single plate is called a quantity arrangement, because it decomposes, with the consumption of a given quantity of zinc and acid, as great an amount of any compound *which it will decompose*, as the other arrangement decomposes, by an equal consumption of materials, in *each* cell of the battery; but there are very few compounds which may be resolved into their constituent elements by a single pair. A case will perhaps make the matter more clear. Suppose we have a battery consisting of ten cells, and that water be made the medium of communication between its extremes, as much water will be decomposed by this instrument as by one of a hundred pairs supposing them to be similarly circumstanced in every respect. This at first sight appears paradoxical, but an examination of the nature of the chemical action in the voltaic battery will remove every difficulty.

Before proceeding to this examination, it is necessary to allude to the subject of chemical equivalents. Suppose four elements, A, B, C, D, to be capable of combining together so as to form a variety of compounds; and suppose, further, that one part by weight of A, combined by two parts

of B, to form a compound, with three of C to form another, and with four of D to form a third. Now it is found that these numbers not only represent the proportions in which these bodies combine with A, but also the proportions in which they combine with each other. For example, if there exist a compound formed by the union of B and C, the proportions of those elements will be represented by the numbers above associated with them; namely, two of the former and three of the latter, or some multiple of those numbers. Further, the proportion of any one of these elements represented by its number, is chemically equivalent to the proportion of either of the other elements, represented by its number; thus, if a compound consisting of three parts of C, and four of D, be decomposed by the addition of the element A, the proportion of this last element requisite for such decomposition is represented by 1, which will combine with 3 of C, or 4 of D, and by that combination will liberate 3 of the former, or 4 of the latter, as the case may be. It is evident then, that 1 of A is equal to—inasmuch as it takes the place of—4 of D or 3 of C in a chemical compound, and *vice versâ*. These combining numbers of the various elementary bodies, are called their chemical equivalents.

We shall now see how beautifully the phenomena of voltaic electricity accord with this definite chemical action. The annexed diagram, *fig.* 5, represents a single voltaic pair, consisting of a plate of zinc, *a*, and another of copper, *b*, immersed in a vessel of dilute sulphuric acid; a wire from the zinc is connected with a plate of platinum *c* in a second vessel, containing dilute acid; and a wire from the copper is attached to another plate of platinum *d*, also in the acid solution. It has already been said that a single pair will not decompose water, but in this illustration we will suppose that it possesses that power (for by a slight modification it may be made to do so), as we prefer that, in this experiment, water should be the compound decomposed. The voltaic current, then, originating at the surface of the zinc, gives rise to the combination of oxygen with that metal; while hydrogen escapes at the surface of the copper; we will suppose the current passing from the copper through its wire to the platinum plate in the second vessel, thence through the liquid to the other platinum plate, and through its wire to the zinc.

Fig. 5.



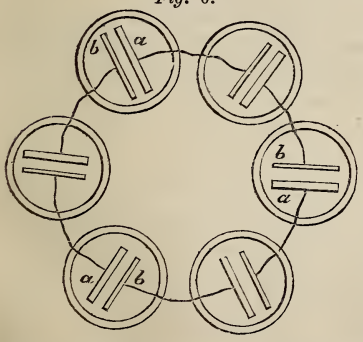
Now, in tracing the current through the battery, it will be observed, that oxygen is that element of the decomposed water which occurs at the surface from which the current enters the liquid; and that hydrogen, the other element of water, is disengaged at the surface where the current leaves the liquid—namely, the copper; on examining the decomposition in the second cell, precisely the same thing occurs, oxygen is liberated at the surface of that platinum connected with the copper, and at which the current enters, and hydrogen at the other plate, or that surface where the current leaves the

liquid; nay, further, the quantity of water decomposed in the second cell, is exactly equal to the quantity decomposed in the battery; the hydrogen is equal in volume to that given off in the battery, and the oxygen equal to that which has combined with the zinc. We must here repeat, that we have assumed, for the purpose of explanation, that which is not strictly correct; inasmuch as a single cell will not decompose water, except under circumstances which we have not introduced into the experiment: but other substances may be decomposed by such an apparatus, and the results are in perfect accordance with what has been said: an amount of such compound will be decomposed, chemically equivalent to the amount of water decomposed in the battery: our reason for putting the experiment in the above form is, that no misconception may arise respecting the chemical action of voltaic electricity, for the decomposition of the same compound has been effected both in the battery and in the secondary cell; and the amounts of such decompositions, not, as they must have been with dissimilar compounds, relatively, but absolutely the same.

We will now proceed to a consideration of the compound battery, and in that instrument we shall have a further confirmation of the view we have been endeavouring to enforce, that the voltaic current, in passing through any solution, effects the same amount of decomposition as is effected in the battery itself.

The annexed diagram, *fig.* 6, will serve to illustrate the nature of the compound battery,—to explain the cause of the intensity of such a modification,—and to reconcile the apparent anomaly that such an arrangement evolves a current no greater in quantity than that generated by any one of its cells. The apparatus represented consists of a series of cells, each containing a plate of zinc, *a*, and another of copper, *b*, immersed in dilute sulphuric acid, the zinc of one cell being joined to the copper of the next. An apparatus situated as the above would be extremely active; the evolution of hydrogen would be very copious, and the zinc would rapidly dissolve, for there is no obstruction to the passage of the voltaic current. To begin our illustration, let the reader imagine, in the first instance, that only one of the cells of this compound battery is in action; it is immaterial which is selected; the current of electricity generated in that cell has to pass through each of the others; and, as we have before shown, in passing through the dilute acid, the water of that acid will be decomposed, oxygen will be developed at the surfaces where the current enters, and hydrogen at the surfaces

Fig. 6.



where it leaves the solution; so that this current, supposing it capable of passing through a hundred such cells, would decompose in each as much water as was decomposed in the battery. Now this current meets no obstruction whatever in passing through the arrangement described; on the contrary, it acquires an additional impulse at every cell, for each one, being precisely similar to that from which the current was supposed to originate, is equally favourable to the passage of a voltaic current; and hence such current is accompanied by a given amount of chemical action in its passage through each cell, and acquires thereby additional intensity. In other words, each cell of a compound battery is a decomposition cell, in which the materials are so arranged that, instead of obstructing the passage of the current, there is a disposition to the generation of one. The reader will now perceive the cause of the intensity of the compound battery, and, recollecting that the same current effects the decomposition in each cell, will no longer be surprised that the quantity of electricity in a compound battery is no greater than that of one of its cells.

If any one of the wires connecting the plates of the last described apparatus be severed, and the cells be ranged in a straight line instead of a circle, it will immediately be recognised as the *couronne des tasses* of Volta, described in an early part of this treatise; the wires which now constitute the ends of the apparatus, are what have been very inappropriately termed the poles of the battery. After what has been said, it is hardly necessary to remark that, by plunging them in water, the circuit being again completed, the action of the battery recommences, and the water will be decomposed. It was formerly believed that the decomposing power of the voltaic battery was owing to an attraction existing between these wires and the elements of the compound; it is evident that such a view is incompatible with the present state of science; still, however, the terminal wires of a battery are called the positive and negative poles. Many attempts have been made to introduce less objectionable names, but they have been only partially successful. It was proposed by Farraday to call them electrodes, or passages for the electricity; the one being distinguished as the *anode* and the other as the *cathode*, in reference to the presumed direction of the current. It has also been advised to call them the zincode and platinode; and a third party has named them oxode and hydrode. The reader will bear in mind that the words negative pole, cathode, and platinode are synonymous, and are employed to designate the plate or metal, which, considering the decomposition cell as one of the cells of the battery, holds the place of the copper, silver, or platinum; and that the positive pole, anode, zincode, or oxode is that at which oxygen, acids, &c., appear, and corresponds with the zinc of the battery.

There are two other circumstances connected with the decomposition effected by the battery, which must be noticed in this place. No solid can suffer decomposition in the voltaic circuit; nor can any fluid excepting

such as conduct—and in them conduction and decomposition are, with few exceptions, inseparable. For example, chloride of silver is, at ordinary temperatures, a solid—and in that state resists decomposition by the most powerful apparatus; by the application of heat, this compound fuses, and in that state conducts the current even of the feeblest voltaic arrangement, and, at the same time, suffers decomposition. Water affords an illustration still more striking. In its ordinary, or fluid state, it is decomposed by a current of moderate intensity; but when frozen the utmost intensity will not effect the separation of its elements; for in such a state it does not conduct the voltaic current. If one of the platinum plates in the apparatus be coated with the thinnest film of ice, it will effectually stop the current.

There are apparent exceptions to both these laws. Experiments have been adduced in which compounds, in the solid state, appear to have been decomposed, and in which fluids have conducted without decomposition.

Many of the changes which occur in the voltaic circuit are due to what is called secondary action; in the case of aqueous solutions, many of the decompositions may be traced to the action of the oxygen and hydrogen, evolved by the passage of the current through the water, and are independent of the voltaic power. The precipitation of the metals by voltaic electricity is generally to be ascribed to a secondary action, as will be explained hereafter—though there are cases in which the elements of a salt are separated by the direct action of the current. This direct action of the voltaic current is, however, very limited, as only compounds of a particular constitution are susceptible of such decomposition; and this constitution not with regard to the elements, but the proportion of those elements; for of two compounds, formed of the same elements, one may suffer decomposition, and the other resist it.

Only those compounds consisting of one equivalent or proportion of each element are affected by the voltaic current. It is not, however, essential that the elements should be simple, undecomposable bodies; for a body whose elements are compounds suffers decomposition, or is resolved into those proximate elements; and these elements themselves may even be so constituted as not to yield up their component parts in the voltaic circuit. Examples will impress this law upon the memory. Water is a compound of one atom or proportion of each of its elements, and, consequently, in accordance with the law above stated, is decomposed by the voltaic battery. But any compound of the same elements in a different proportion would not suffer decomposition. If there were a compound of two atoms of hydrogen and one of oxygen, it would not be affected by voltaic electricity. And so with those substances whose constituent parts are compounds; in order to suffer decomposition by the voltaic current, they must consist of one equivalent, or proportion, of each of their component elements. Sulphate of copper, for example, is resolved into sulphuric acid and oxide of copper; though the

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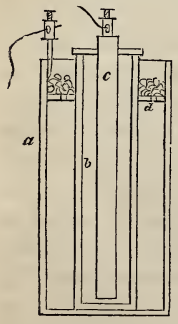
sulphuric acid will not, under similar circumstances, be decomposed, for it is not a binary compound; nor will oxide of copper, inasmuch as it is a solid.*

Having explained the action of the voltaic battery, we will proceed to notice the improvements which have been introduced in that instrument subsequent to the one we last described—namely, the amalgamation of the zinc plates. Long prior to the invention of Professor Daniell (which comes next in order) it was known that, by increasing the size of the negative plate of the battery, there was a considerable increase in the quantity of electricity generated. The reader will recollect that Dr. Wollaston's improvement consisted in surrounding the zinc with copper, and that that instrument was superior to those in which a less negative metal was used; but there is obviously a limit to this extension of the negative plate; for, by enlarging it, it necessarily becomes removed to a greater distance from the zinc, and thereby defeats its object; for with negative plates of given size, it will be found that the evolution of hydrogen rapidly diminishes as it is made to recede from the zinc, and *vice versâ*. However large the negative plate is made—when in action, it is, virtually, exceedingly small; as we have already seen, the moment the action of the battery commences, that plate becomes covered with bubbles of hydrogen, and the parts so coated, being defended from the liquid, are for the time inactive; hence the extent of metal which is in constant contact with the liquid is exceedingly small, owing to this evolution of hydrogen. This defect is completely remedied by that arrangement of the battery devised by Professor Daniell, and called by him the "constant battery." The grand principle in this instrument is the placing of a solution of sulphate of copper in contact with the copper of the battery, whereby the hydrogen presented at that surface is made to enter into chemical union with the oxygen of the sulphate of copper, while in its nascent state; and by the suppression of that gas, a large and constant extent of negative surface is exposed to the zinc. A single cell of the constant battery is represented in section in *fig.* 7. It consists of an outer cylindrical copper vessel, *a*, of about three inches diameter, and of any convenient height; in the axis of this cylinder is placed a cylindrical vessel of porous or unglazed earthenware, *b*; and in this porous vessel is suspended a rod or cylinder of amalgamated zinc, *c*; dilute sulphuric acid is placed in the interior or porous vessel, and a saturated solution of sulphate of copper in the exterior, or copper vessel. The action of the sulphuric acid on the zinc the reader is already familiar with; and as the

Fig. 7.



* Other views of voltaic decomposition have been advanced, but, as they involve a theoretical constitution of the salts different from that here given, and at present generally entertained, it is unnecessary to do more than thus allude to them.

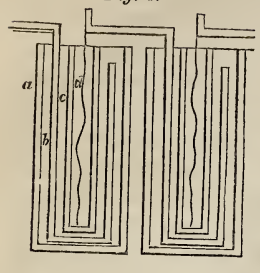
use of the porous cell is simply to prevent the mixture of the two solutions, by interposing between them a substance which will not materially interfere with the passage of an electric current through them, we may altogether dismiss it in considering the phenomena which take place. The hydrogen then passes freely to the copper cylinder or negative plate, and is there evolved; on coming in contact with the metallic solution while in its nascent state, (that is before it has assumed the gaseous form) it decomposes that solution, by combining with the oxygen of the metallic salt. Sulphate of copper is composed of sulphuric acid and oxide of copper; the latter consisting, as its name indicates, of oxygen and metallic copper. The hydrogen combines with the oxygen of the oxide, and thereby forms water, and metallic copper and sulphuric acid are liberated. The metallic copper thus precipitated attaches itself closely to the copper cylinder, in which the solution is contained; and this cylinder constantly increases in thickness during the action of the battery by this accumulation of the deposited copper. Crystals of the sulphate of copper are laid upon a perforated shelf, *d*, fixed in the upper part of the cylinder, which keep the solution always saturated. By the means now described the evolution of hydrogen at the surface of the negative metal, which has been shown to be so disadvantageous, is completely suppressed; and by the copper or negative surface being separated from the solution of sulphate of zinc formed in the interior vessel; that reduction of zinc upon it, which occasions a diminution of power in the ordinary battery, is completely avoided.

This voltaic arrangement produces a current of greater intensity than any preceding it; added to which, it possesses the valuable property of extreme uniformity of action—insomuch that a current having an invariable intensity, may be secured for many hours, by the use of this instrument. We must not, however, omit to mention the disadvantages which are peculiar to it. The expense of the salt of copper renders it less economical than other forms of battery; the porous cells are liable to break after use by the crystallization of the saline matter contained in their pores, and from which repeated washings scarcely suffice to free them. A very small extent of zinc surface is exposed; and, as the instrument is inactive until the solutions have penetrated the porous cell, it requires longer time to bring it into active operation than most of the other forms of battery. We repeat, however, that it has valuable porperties not possessed by any other instrument.

Subsequent to the invention of Professor Daniell is that of Mr. Grove—an instrument which far surpasses all that preceded it in point of intensity. In principle it is precisely similar to that of Professor Daniell; the hydrogen is suppressed at the negative plate by being presented to concentrated nitric acid; and, in order that the acid may have no action on that plate, Mr. Grove uses platinum. It is hardly necessary to remark that the hydrogen decomposes the nitric acid by combining with its

oxygen. *Fig.* 8 is a sectional representation of two cells of Grove's battery; *a* is the outer cell of glazed earthenware; *b*, a plate of zinc beat into the form represented; *c*, a vessel of unglazed earthenware; *d*, the plate of platina. The vessel *a* is charged with dilute sulphuric acid, in the proportion of one of concentrated acid to seven of water; the vessel *c* is filled with concentrated nitric acid. The advantages attendant on this battery are its extreme activity and the intensity of the current generated; a single cell of this arrangement decomposes water, and a battery of three or four cells possesses intensity enough for all ordinary purposes; the disadvantages under which it labours are, that its power is transient, and that the evolution of nitrous fumes renders it exceedingly offensive. The expense of the nitric acid is also an objection.

Fig. 8.



From what has been previously said respecting the intensity of the voltaic batteries, the reader will, perhaps, be somewhat surprised at the remark, that Daniell's battery possesses a greater intensity than is produced by a simple acid battery, and that a single pair of plates, arranged on Grove's principle, will decompose water. It is nevertheless true, that the intensity of a single pair of voltaic elements is increased in a surprising degree by the application, either of the solution of the sulphate of copper, or concentrated nitric acid, to the negative plate. The following experiment will illustrate this fact:—take a single cell of Grove's battery, and connect the platinum and zinc with two platinum plates immersed in dilute acid, as shown in *fig.* 4. Let the battery be partly filled with dilute sulphuric acid, and let a quantity of the same be put in the porous cell. No action will take place; the current will not pass through the acid in the second cell, and the water, consequently, will not be decomposed. Without disturbing the arrangement, introduce some concentrated nitric acid into the porous cell, and the platinum plates in the second cell will immediately evolve—the one oxygen, the other hydrogen—and these gases will continue to be given off until all the nitric acid in the battery has been decomposed by the hydrogen evolved in it—demonstrating that the current has, by the introduction of the nitric acid, acquired an intensity much greater than it previously had.

It is by no means easy to understand the cause of this intensity; the most plausible theory which has been proposed is, perhaps, the following:—the intensity of the current in the simple acid battery may be represented by the attraction of the oxygen of the water for the zinc; in Daniell's battery, the attraction of the oxygen for the zinc, plus the attraction of the hydrogen for the oxygen of the oxide of copper, minus the attraction of that oxygen for the metallic copper with which it is combined; and in Grove's battery the intensity will be represented by

the attraction of the oxygen of the water for the zinc, plus the attraction of the hydrogen at the negative plate for the oxygen of the nitric acid, minus the attraction of that oxygen for the nitrogen with which it is combined.

The only other modification of the battery we have to notice is the arrangement of Mr. Smee. In order to avoid the expense attendant on the removal of the hydrogen by chemical means in the batteries just described, Mr. Smee endeavours to effect the same by mechanical means. Having observed, during the evolution of gaseous matter from different plates, that the bubbles of gas adhere very tenaciously to smooth surfaces, but are, on the contrary, quickly liberated from roughened ones, Mr. Smee gives the negative plate of his battery an infinity of minute points exceedingly favourable to the rapid evolution of gas, by precipitating upon its surface the metal platinum in a finely divided state. The way in which this is effected will be understood by a perusal of the subsequent pages of this treatise. The battery of Mr. Smee differs only from those used long before the inventions of Daniell and Grove, in this preparation of the negative plate; and, like them, is excited by dilute acid only.*

Before dismissing the subject of voltaic batteries, we would remark, that whatever form is given to an instrument of this kind, the amount of electricity generated by the consumption of a given amount of zinc is the same in each; they differ only in the rapidity with which the developement of the voltaic power takes place. In the invention of Daniell a flow of electricity of extra uniformity is produced. We have a torrent of surprising intensity, but of transient duration, in the battery of Mr. Grove; and a copious flow of electricity of moderate intensity in the common acid battery and that of Mr. Smee: but we repeat (for it cannot be too strongly urged upon the reader) that in all these instruments a like amount of this subtle agent is obtained by a like consumption of materials,

* Since the above was written, the battery of M. de Moleyns has been made public. It consists of an arrangement exactly similar to that of Mr. Grove, but is excited differently. The external cell containing the zinc is filled with a saturated solution of muriate (hydro-chlorate) of ammonia (sal ammoniac,) and the internal porous cell in which the platinum is placed is filled with a solution prepared in the following manner:—Dissolve one pound of nitrate of ammonia in a pint of water; place the vessel containing the solution in a frigorific mixture, and add slowly an equal quantity of concentrated sulphuric acid. This battery possesses an intensity equal to that of Mr. Grove's; and the inventor states that its advantages are—the length of time it continues in action; the intensity it possesses; and, as the zinc plates need not be amalgamated, he claims that as one of its advantages. The last, however, is not peculiar to his battery. The solution of muriate (hydro-chlorate) of ammoniate is commonly employed in Daniell's battery instead of the dilute acid, and in that case the zinc is not amalgamated; and I have made many experiments with Grove's battery in which I have employed a saturative solution of the salt in question in lieu of the dilute acid, and the effect has certainly not been diminished by the substitution; nay, in the few comparative experiments I have made on the subject, there appears to be a considerable increase of power; for, with two batteries of exactly the same size, one charged with dilute sulphuric acid in contact with the amalgamated zinc, and the other with the saturated solution of muriate of ammonia and unamalgamated zinc, the latter gave in eight minutes a volume of the mixed gases from the decomposition of water equal to that produced by the former in nine minutes and a-half.—G. S.

the intensity alone being affected by the arrangements of Daniell and Grove. In Smee's battery this is not at all increased; the mechanical form of the surface of the negative only facilitates the escape of the hydrogen therefrom.

Having said thus much respecting the history of the Voltaic Battery, we will at once proceed to that of the Electrotype. It has been already several times remarked, that in Daniell's battery metallic copper is precipitated on the copper cylinder containing the solution of the sulphate of that metal. This precipitated copper is not very intimately attached; for, by the application of a moderated force, it may be torn off. This fact was known to Mr. Daniell, who showed that the detached metal had been deposited in such close contact with the matrix, that it exhibited impressions of marks on the latter with extreme fidelity: he did not think, however, of applying this fact to any useful purpose. In the course of experiments made with this battery, other philosophers observed the same fact. In October, 1838, Professor Jacobi announced that he could employ the voltaic battery in the reduction of copper for various purposes; and to his art was given the name of Volta-Plastics. Immediately this was made known in England, Mr. Spencer, of Liverpool, announced that he had copied medals by the agency of voltaic electricity; and to the apparatus he employed was given the name of Electrotype.

Mr. Spencer's first communication to the public was on the 12th of September, 1839. His paper was to have been read at the meeting of the British Association in Birmingham; but for some unexplained reason, it was not called on: it was subsequently read before the members of the Liverpool Polytechnic Society, on the day above specified. In this paper (which was afterwards published) Mr. Spencer details the circumstances which suggested to him this application of voltaic electricity. He observed, during one of his experiments, that a copper plate, which he had been using as a negative element in a voltaic arrangement, in which the solution of sulphate of copper was employed, had become covered with the precipitated metal in every part, excepting two or three places, where, by accident, some drops of varnish had fallen; it immediately occurred to him that if a plate of varnished copper, having a design made upon it by a pointed instrument, so as to remove the varnish, were made the negative plate of a voltaic arrangement, that copper would be precipitated on the parts were the metal was exposed; so that, on removing the varnish, the design would be left in relief.

This mode of voltaic engraving is not likely to come into general use, as many difficulties attend the execution of it. In the same paper Mr. Spencer relates another experiment that suggested to him that application of voltaic electricity which is at present known as Electrotype. "The members of the society," says Mr. Spencer, alluding to the Liverpool Polytechnic Society, at a meeting of which this paper was read, "will recollect that on the first evening it met I read a paper on the 'Production

of Metallic Veins in the Crust of the Earth;" and that, among other specimens of cupreous crystallization which I produced on that occasion, I exhibited three coins; one wholly covered with metallic crystals, the other on one side only. It was used under the following circumstances:— When about to make the experiment, I had not a slip of copper at hand to form the negative end of my arrangement, and, as a good substitute, I took a penny, and fastened it to one end of the wire, and put it in connection with a piece of zinc in the apparatus already described. Voltaic action took place, and the copper coin became covered with a deposition of copper in a crystalline form. But when about to make another experiment, and being desirous of using the piece of wire used in the first instance, I pulled it off from the coin to which it was attached. In doing this, a piece of the deposited copper came off with it: on examining the under portion of which, I found it contained an exact mould of a part of the head and letters of the coin, as smooth and sharp in every respect as the original on which it was deposited."

We learn, by the above extract, that Mr. Spencer was experimenting with a voltaic arrangement similar to that of Professor Daniell; and that, on detaching the precipitated copper, he found, as that gentleman and others had done, that every impression was transferred to the precipitated copper. It is true, accident presented the fact to him in a much more forcible form than that in which it had been presented to others; the want of a proper piece of copper to complete the arrangement occasioned Mr. S. to introduce a penny as a substitute, and, on detaching the precipitated copper, he found the head and letters distinctly marked upon it; so that a fac simile of the coin was produced, quite unintentionally on the part of Mr. Spencer; and this new application of the voltaic battery was presented to him in a manner so forcible that it was impossible to neglect it. Mr. Spencer pursued the subject, and so far succeeded in his experiments as to be able to furnish processes by which medals and plates may be copied, and some non-conducting substances coated with copper.

Since the experiments of Jacobi and Spencer, many individuals have contributed to the perfection of this novel and interesting art. Among others, the names of Mason, Murray, and Smee, must not be omitted. We cannot, however, do justice to the labours of these gentlemen, until we have given an account of the art as it proceeded from the hands of Mr. Spencer. We shall, therefore, proceed at once to describe that gentleman's apparatus, for the production of copies of coins, medals, plates, &c. The annexed engraving, *fig.* 9, represents the apparatus for procuring fac similes of coins, and medals. *a* is a glass or earthen vessel, containing a saturated solution of sulphate of copper: *b* is a cylinder of glass, the bottom of which is closed by brown paper, plaster of Paris, or bladder; this vessel contains a solution of sulphate of soda, or muriate of ammonia: *c* represents the

Fig. 9.

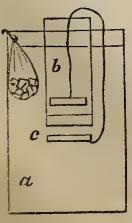
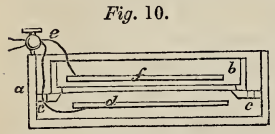


plate or mould on which the deposit of metallic copper is to be received; a wire, fixed by soldering or otherwise to this mould, is connected with a piece of zinc placed in the saline solution in the glass cylinder *b*. To set this apparatus in action, the outer vessel is filled with the cupreous solution, and some crystals of sulphate of copper are suspended in the upper part of the vessel, either on a perforated metallic shelf, or in a piece of muslin, to keep the solution saturated, as the decomposition of the salt is continually going on during the working of the apparatus; the saline solution being put into the glass cylinder in which the zinc is situated, completes the preparation. If the metallic communication between the zinc and the mould be perfect, action immediately commences; the mould becomes almost instantly covered with a stratum of copper, which goes on increasing in thickness so long as the strength of the cupreous solution is maintained. The rapidity of the deposition is determined by the nature of the porous material with which the bottom of the glass cylinder is closed. If it is of brown paper, the deposition goes on with considerable rapidity; bladder occasions a slower deposition; and plaster of Paris retards the process still more; the thickness of the various materials also influences the action, it being most intense when the interposed diaphragm is thinnest. From what has been said respecting Daniell's battery, the reader will easily understand the nature of the action, and the cause of the changes which take place in this apparatus.

Fig. 10 represents an apparatus for manufacturing copper plates, as described by Mr. Spencer:—*a* is a box, which may be made either of earthenware, wood, or glass, and of any size which may be found convenient; *b* a box, of either of the above materials, but having a thick brown paper or thin unglazed earthenware bottom, the sides being impermeable by a fluid. This must be made to go into the interior of *a*, and to rest on the rim *c c*, running round the interior of the larger box, taking care, at the same time, that there shall be an inch or more of free space, according to the size of the apparatus, between the exterior of the small box and the interior sides of the larger one. The rim *c c* must be perforated with small holes, and it must be made to support a supply of crystals of sulphate of copper; *d*, the plate to be deposited on, to which a wire is attached, leading to the binding screw, *e*, fastened to the top of the exterior box; *f*, the plate of zinc, to which a wire is attached, also leading to the binding screw. The connection between the two plates is thus rendered perfect, and either may be conveniently removed without disturbing the other. A few projecting studs of wire on the sides of the interior box, are also found useful, to keep the zinc plate perfectly parallel, and to prevent it from touching the porous bottom. They must be varnished, to prevent local action; or, if the vessel be made of earthenware, they may be attached to the sides in the first instance, and be of the same material. The plate to be deposited

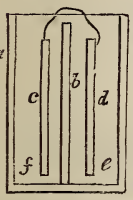
Fig. 10.



on may be kept in its place by similar studs or moveable pieces of earthenware. "The ends of the wires must all be brightened before they are pressed together by the binding screws. When all is arranged, as shown in the figure, pour into the outer box a saturated solution of sulphate of copper until it is nearly full, and then pour into the interior one containing the zinc a weak solution of sulphate of zinc. At this stage of the proceedings, let a quantity of the undissolved crystals of sulphate of copper be placed on the perforated rim. Should this be neglected for any length of time, a brown powder will be deposited on the plate instead of the pure metal. This substance is the protoxide of copper, and always will be precipitated when the liquid is not kept thoroughly saturated with sulphate of copper. In summer the deposition goes on much quicker than when the weather is cold, as heat very much facilitates chemical decomposition." The above extracts will suffice to show the state of the art as it proceeded from the hands of Mr. Spencer.

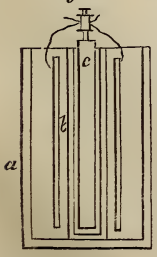
A very convenient form of apparatus is represented in *fig.* 11. It consists of a trough *a*, made of porcelain or varnished wood. It is divided into two parts by a partition of unglazed earthenware or plaster of Paris *b*. The zinc plate *c* is placed in the compartment *f*, containing the dilute acid or solution of muriate of ammonia to act upon it; and into the other compartment *e* is placed the saturated solution of sulphate of copper, to which a little sulphuric acid has been added; crystals of the sulphate must be suspended in the upper part of the latter compartment, in order to maintain the saturation of the liquid. In this compartment the plate *d* to receive the deposit is placed, and is connected to the zinc *c* by a wire.

Fig. 11.



Another, and in some cases more convenient arrangement, is shown in *fig.* 12, where *a* is a cell of earthenware or water-tight wood, in the middle of which is placed a porous or unglazed earthenware cell *b*, the latter is filled with the dilute acid or saline solution, and contains the zinc plate *c*, and the former is filled with the acidulated cupreous solution; crystals being suspended in its upper part, as in all other modifications of this apparatus. Into the outer vessel *a* the plates to receive the coating of copper are situated. The peculiarity in this apparatus is that two surfaces, each as large as the zinc, can be experimented upon at the same time. The connection of the copper plates with the zinc is so evident from the figure that it needs no description. When dilute sulphuric acid is used in any of the instruments described, the zinc immersed in it must be amalgamated; but where solutions of muriate of ammonia or sulphate of soda are used, the amalgamation of the zinc is unnecessary.

Fig. 12.

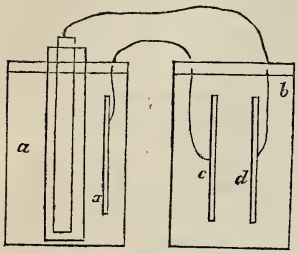


Immediately after the publication of Mr. Spencer's paper, an important improvement was announced by Mr. Mason, in which a great economy is

effected. Mr. Mason used an apparatus exactly similar to that of Mr. Spencer; but, instead of connecting together the zinc and the metal on which the deposit was to take place, he effected a communication through a second vessel, in which, by the passage of the voltaic current, a quantity of copper was precipitated, equal in amount to that precipitated in the primary cell. The process took somewhat longer time, but on the whole, was much more economical than any which preceded it.

In order to make this improvement intelligible, a figure *(fig.* 13*)* is subjoined:—*a* is the common single cell apparatus; the wire from the zinc, instead of communicating directly with the mould, is conducted into the vessel *b*, and is joined to the mould *d;* the mould *x* in the primary cell is connected with a piece of copper *c* in the cell *b*. Now, the current of electricity, in passing through this arrangement, causes the deposition of copper to take place upon the moulds *x* and *d;* but in order that the *modus operandi* of this instrument may be more clear, we shall again refer to the voltaic battery, and examine the nature of the chemical action of that instrument.

Fig. 13.



Let us imagine, then, that we have in the following experiments a battery of sufficient power to decompose water. If the terminal wires of this battery, which we will suppose to be made of the metal platinum, be introduced into acidulated water, we shall observe gas escape from them, and by examination, we further find that the water is decomposed, and that oxygen is evolved at one wire, and hydrogen at the other. If the experiment be varied by the introduction of a solution of sulphate of copper into the acidulated water, a remarkable change in the products of the decomposition will take place. We shall now find that only one wire evolves gas, and that that gas is oxygen. On examining the other wire, where the hydrogen was evolved, we shall observe it to be covered with metallic copper: by continuing the experiment, the precipitated metal will gradually accumulate, the solution will become paler, and at length colourless. When this happens, the whole of the copper will have been precipitated, and hydrogen will be again evolved from the surface of the newly-deposited metal. We see, then, that, by passing a voltaic current through a metallic solution, the hydrogen evolved by the decomposition of the water, effects the reduction of the metal; it combines with the oxygen of the metallic oxide, thereby forming water, while the metal with which it was united is deposited, and attaches itself to the surface at which the hydrogen escaped; the acid which was combined with the oxide to form the salt, remains in solution.

We will now consider what takes place when the wire or surface from which the oxygen is evolved is made of a metal that combines readily with oxygen—we will suppose copper. We shall observe that the

hydrogen is evolved as usual, but that, in the place of oxygen, a brown powder will accumulate about the wire; the latter rapidly diminishes in size, and, by continuing the experiment a sufficient length of time, the whole of that part which was immersed in the water will disappear, and the action of the battery, through the interruption of the circuit, will cease. The brown powder which appears is oxide of copper, and is formed by the combination of the oxygen with the copper of the electrode.

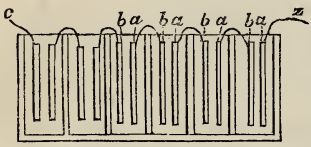
We will next suppose that we immerse two copper wires, or plates, connected with a voltaic battery in a solution of sulphate of copper. We have already seen that a plate from which hydrogen is evolved receives a deposit of copper when immersed in such a solution; and we have also seen that a copper wire, or plate, when oxygen is evolved, combines with that element, forming oxide of copper. Now, as the oxygen evolved at one of the wires is chemically equivalent to the hydrogen liberated at the other, the quantity of oxide of copper formed by the combination of the oxygen with the copper of the former electrode, is exactly equal to that decomposed by the hydrogen at the latter; hence, in the experiment under consideration, there is no visible evolution of gas at either of the wires, the only effect produced being the formation of oxide of copper at one of them, and its reduction on the other, and, consequently, the transfer of metallic copper from one wire to the other. We will now observe these changes as they take place in the apparatus of Mr. Mason. We may suppose that the voltaic current originates at the surface of the zinc, and determines the formation of oxide of that metal; passing to the second cell, it is accompanied by the evolution of hydrogen at the plate, *d*, and metal is deposited thereon; the current, travelling through the liquid to the second plate, *c*, developes oxygen, which, combining with the copper, forms oxide; passing from this cell to the first, it again occasions the evolution of hydrogen, and a second deposition of metal is effected on *x*; the current completes its course by passing again to the zinc. In this arrangement of the electrotype apparatus a double quantity of the reduced metal is obtained.

It is necessary to explain what will otherwise appear a discrepancy. We have supposed the use of a compound battery in our illustrative experiment, though the cell which in Mr. Mason's apparatus generates the electricity is but a single one. The following fact explains the cause of this difference:—It requires considerable intensity to decompose water, if platinum or gold electrodes or poles are used; and in such a case the elements of the water are delivered in a pure form; but where the arrangements are such that the elements enter into combination before assuming the gaseous form, the intensity required for that decomposition is less; the intensity of the current seems to be augmented by the affinity between the oxygen and hydrogen, and the elements with which they are combining. We have seen that a single voltaic pair will determine a current through a solution of sulphate of copper, if the electrodes are of

copper, though a series is required to decompose water with platinum electrodes; in the former case the evolved elements enter into combination, in the latter they do not.

It will immediately occur to the reader that if, by the voltaic battery entering the solution in the second cell, copper is reduced, and by its passage from that cell an equal amount of that metal is taken into the solution, that by causing it to pass through a series of such cells, a similar quantity of copper will be reduced in each; such is exactly the case; and it is now common to cause the completion of the voltaic circuit to take place through six, or even more of such cells, and thus obtain, at a given expense of zinc, six times the quantity of copper that would be obtained by the single cell apparatus. The process goes on much more slowly than if a single decomposition were being effected; but the great saving in the consumption of material is more than sufficient to warrant the adoption of this plan. This arrangement is shown in *fig.* 14, where *a a* are the moulds on which the deposit is to take place, and *b b* pieces of copper to be dissolved. It is necessary to place the mould and copper plate very near to each other, and parallel, as represented in the figure; and they should be as nearly of a size as may be.

Fig. 14.



The cell, *a*, in Mr. Mason's apparatus, is, strictly speaking, a voltaic battery, and, although it *may* be used, as represented in the sketch, as an electrotype apparatus, by its negative plate being a mould on which a deposit of copper is to be effected; yet by far the most convenient plan, and, perhaps, even the most economical one, is to substitute for the cell, *a*, in the arrangement represented, an ordinary voltaic battery; indeed the apparatus now used for electrotype purposes, to the exclusion of almost every other, is that now recommended. The improvement introduced by Mr. Mason possesses such advantages, that the single cell apparatus described by Mr. Spencer has already fallen into very general disuse. By generating the voltaic electricity in an apparatus distinct from that in which the precipitation of the metal takes place, a much greater command over the process is obtained, and the flow of electricity can be regulated with much greater nicety than when the mould to be deposited upon constitutes one of the elements of the battery. It is evident, too, that as the solution in the second, or decomposing cell, is always of the same degree of concentration, the experiment, when once adjusted, may be suffered to proceed, without risk of failure from any change in the nature of the solution. Another convenience attending this mode of procedure is its simplicity. In Spencer's apparatus, the solution of sulphate of copper is suffering continual loss of the salt owing to its decomposition, and it is necessary to replenish the solution by the suspension of crystals of sulphate of copper in the upper part of the vessel; but in

Mr. Mason's apparatus it is only necessary to use so much sulphate of copper as is sufficient to form the original solutions; for, as has been shown, the solution is not at all affected by use, and is in precisely the same state of concentration throughout the longest process in which it may be employed.

We have now so far treated of the general principles of the electrotype, that we may proceed to a more detailed account of the art, and its application in various ways. The nature of the surfaces on which a deposit of copper may take place in the electrotype demands our first attention. After what has been said, we need scarcely remark that the deposition of copper takes place with great facility upon the surface of any metal which is not chemically attacked by the solution into which it is necessary to plunge it. We may, therefore, in copying coins, medals, or plates, introduce them at once into the solution, and, by procuring a deposit upon them, obtain a mould, which will afterwards serve to receive another deposit, the fac simile of the medal. It is necessary to remark that the bronze appearance of a medal is sometimes injured by this mode of proceeding; of all methods of copying coins or medals by the electrotype it is the worst, and should only be adopted in those cases where slight injury to the coin or medal is unimportant. A much better way is to take moulds of the coin or medal, and procure a deposit in them. In copying engraved plates, or large subjects whose surfaces are not of so delicate a nature as those of medals, the above process is, however, exceedingly convenient.

Many precautions are necessary in order to prevent the adhesion of the precipitated copper to that on which it is deposited. If the wire which connects the plate to the battery has been soldered to it, or the plate otherwise heated, it is essential to allow it to remain many hours exposed to the air in a cool situation; for if it be introduced into the apparatus immediately after having been heated, the precipitated copper will adhere so as to resist all attempts to remove it; but, after the treatment above recommended, there is much less disposition to adhesion; still, the introduction of a plate into the apparatus, under such circumstances, is not unattended with danger; and it is advisable always to adopt the simple and efficacious plan recommended by Mr. Spencer, which will be found perfectly effectual in preventing the adhesion of the deposit. The plate on which the deposit is to take place should be heated and rubbed with bees' wax until every part has received a coating; the wax should be thoroughly melted, and, after having remained a few minutes on the plate, may be carefully wiped off with a linen rag; when cold, it may be introduced into the electrotype apparatus without fear of adhesion. In cleaning the wax from the plate care should be taken not to leave any portion uncleaned; in such a case no deposit will take place on the part coated with the wax. Where the surface of the plate to be deposited upon is not of extreme delicacy, the following method may be adopted for preventing the adhesion:—the plate should be immersed in

some solution that will deposit upon it a thin film of a dissimilar metal—the cyanide of silver, for example, which, in a few seconds, will give it a thin coating of silver, or it may be connected with the battery, as hereafter described, so as to obtain a thin coating of that metal; the deposited copper, being separated from the original plate by a thin film of silver, will readily separate; copper reduced in the electrotype may become one with the copper on which it is deposited, or silver with silver; but dissimilar metals are with difficulty made to unite firmly.

For small plates and coins, moulds may be readily made in lead, and there is no risk of adhesion between this metal and the copper; such moulds need no preparation. If the medal, or other subject to be copied, is not very prominent, impressions of either side (in case of a medal) may be procured by simply placing it between two pieces of sheet lead, the surfaces of which have previously been made clean by scraping, and subjecting it to the action of a pur. Mr. Spencer suggests that a number of coins be placed between two strips of lead, and these passed through a copper-plate printer's press. A series of impressions will thus be produced, and, by placing these strips in the voltaic apparatus, a sheet of electrotype casts will be obtained, or, by varnishing the space between the impressions, they will be separated. This plan, however, will not succeed in subjects whose surfaces are prominent. Moulds from these must be obtained by casting, either in fusible alloy, wax, plaster of Paris, &c. The alloy known by the name of Newton's fusible metal, and consisting of about eight parts of bismuth, four of tin, and five of lead, may be used, but the composition will be much improved if one part of antimony be added; this mixture must be melted repeatedly, and poured in drops, in order to effect a perfect uniformity in the composition. It fuses at a low temperature, and a lamp is a very convenient means of melting it in small quantities. In using this alloy, it is well to melt it with the application of as little heat as possible, and, after having stirred it, to pour a quantity either upon paper placed upon a flat surface, or into a non-metallic surface, slightly concave. It may be stirred about with cards until it approaches the solidifying point, when the medal is to be pressed upon it in the manner which will be hereafter described. The stirring, however, is not necessary, for the most perfect casts may be obtained by simply pouring out the metal, and, after having drawn lightly over its surface the smooth edge of a card, held in an inclined position, applying the medal thereto just before it is about to solidify. The exact point of time is essential; if it is placed upon the fluid metal while too hot, the cast will be deficient in that sharpness and brilliant surface essential to perfection—and, if too cold, an imperfect impression will be the result; the moment when the metal is assuming that crystalline arrangement which is the first step to solidification is the best time for the application of the mould. In order to ascertain this time, we have only to look closely at the surface of the fluid metal. At first a picture

of the surrounding objects will be reflected from it with the utmost accuracy; in a few moments the edges of the melted mass appear less bright, and eventually the whole surface partakes of the same character. A number of points appear to be rising upon the surface, and thus destroy the accurate reflection of objects. It is at this stage that the medal should be suddenly brought down upon it in a horizontal position, and with such force as to bury half the thickness of the metal in the alloy. In order to bring the medal down in a horizontal position considerable care is requisite, and, even then, unless assisted by some mechanical contrivance, it is exceedingly difficult. Much of the uncertainty of the process may be removed by attaching the medal to some support, which affords firm hold for the hand—a rod or cylinder of wood for example. It is unnecessary to enlarge on this subject, as a variety of ways of accomplishing the same object will occur to the experimenter.

Moulds of extreme beauty may be made of wax and other similar substances, such as stearine and tallow. Moulds of wax are formed very readily. The medal is slightly smeared with olive oil, and a slip of paper is fastened around it. The melted wax is poured over it, and is allowed to cool. It is desirable to have the medal warmed, and the wax should be allowed to become so cool as to set soon after it is poured on. If either of these conditions be neglected, the experiment will be unsuccessful. If the medal is not warmed the wax will be suddenly chilled, and the mould will present a waved appearance; and, if the wax is used too hot, the oil becomes incorporated with it before setting, and the cast cannot be removed. Casts of plaster medallions may be be taken in wax by a process of extreme simplicity. The plaster model is to be placed in warm water, and allowed to remain there until it ceases to absorb it. It may then be removed, and, after the water has disappeared from its surface, the wax may be poured over it. Immediately it has cooled, it may be removed without the slightest difficulty. Moulds, if thus procured, are of singular beauty; and, if the plaster model has been properly prepared, it is not in the least injured by the application of the warm water. If it be made of bad plaster, small portions of it will probably be detached, and will be found adhering to the wax mould; these may be removed by the application of dilute sulphuric acid; after a short time a camel-hair pencil will clear it away. Moulds may also be formed of plaster of Paris. The manner of operating with this substance is so well known that a detailed account of it is unnecessary. Powdered gypsum, or sulphate of lime, when heated to a proper temperature, possesses the remarkable and valuable property of becoming a hard solid when mixed with water. The powder is mixed with it so as to have the consistence of thick cream, and, after having been well stirred to remove the bubbles arising from the air which had been lodged in the plaster, it is poured on the medal, or object to be copied, which, when necessary, should be slightly oiled. After the lapse of a few minutes, the plaster will be so

hard that it may be safely removed; but it requires a much longer time to attain its greatest hardness.

Moulds or surfaces for electrotype purposes, if made of any other than a metallic substance, require preparation before they are fit for receiving the deposit. This preparation consists in coating the mould with some material which conducts electricity; for wax, plaster of Paris, and other non-metallic substances are (with the single exception of charcoal) non-conductors of electricity, and, consequently, will not receive any deposit in the electrotype apparatus. The various processes which have been given are so effectual that there is nothing more to be desired in this department of the art. Mr. Spencer gives the following account of the modes he adopts:—"I procured two models of an ornament, one made of clay, and the other of plaster of Paris, soaked them for some time in linseed oil, took them out, and suffered them to dry, first getting the oil cleared off the surface. When dry, I gave them a thin coat of mastic varnish. When the varnish was nearly dry, *but not thoroughly so*, I sprinkled some bronze powder on that portion I wished to make a mould of. This powder is principally composed of sulphur and mercury, or it may be chemically termed a sulphuret of mercury. There is a sort that acts much better, in which is a portion of gold. I had, however, a complete metalliferous coating on the surface of the mould, by which I was enabled to deposit a surface of copper on it by the voltaic method I have already described. I have also gilt the surface of a clay model with gold leaf, and have been successful in depositing copper on its surface. There is likewise another and, as I trust it will prove, a simpler method of attaining this object; but, as I have not yet sufficiently tested it by experiment, I shall take another opportunity of describing it." The method here alluded to was afterwards given by Mr. Spencer in the following words:—"To obtain a copper mould, or cast from a piece of wood, plaster, or clay, or indeed any non-metallic material, proceed as follows:—Suppose it to be an engraved wooden block which you are desirous of metallizing, in order that copper may be deposited on its surface—this example holding good for any other material. The first operation is, to take strong alcohol or spirits of turpentine in a glass vessel, and add to it a piece of phosphorus (a common corked phial will answer the purpose); the vessel must now be placed in hot water for a few minutes, and occasionally shaken. By this means the alcohol will take up about a three hundreth of its bulk of phosphorus, and we thus obtain a solution of phosphorus. Next, procure a weak solution of nitrate of silver, place it in a flat dish or saucer; the engraved face of the block must now be dipped in this solution, and let remain for a few seconds to allow capillary attraction to draw the nitrate of silver into the wood. This operation being performed, a small portion of the solution of phosphorus must be placed in a capsule or watch glass, and this be placed on a sand-bath, that it may gradually evaporate. The block must now be

held with its surface over the vapour, and an *immediate change* takes place; the nitrate of silver becomes deoxidized, and gives place to metallic silver, which allows the voltaic deposit to go on with as much rapidity and certainty as the purest silver or copper. The whole process may be performed in a few minutes, and with absolute certainty of success. The interior or exterior surface of a plaster or clay mould of a statue, no matter what size, may be thus metallized with equal facility. For the process of vaporizing, when the material to be acted on is not very large, fasten it to the top of a bell-glass receiver with a bit of pitch or cement, and place it thus over the capsule on the sand-bath; the phosphoric vapour is by this means equally diffused, and not dissipated. A solution of phosphorus in sulphuric ether also answers; and a solution of chloride of gold may be used."

This elegant process, as applied to wood, and those substances which may be wetted with the solution of nitrate of silver, answers perfectly; but it is obviously limited in its application to those substances which will absorb an aqueous solution. The process of Mr. Murray is by far the best which has yet been made known for rendering the surface of non-conducting substances capable of receiving the deposit. It consists in covering the surface of the mould with plumbago, or, as it is commonly called, black lead. If the mould or surface is of wax, all that is necessary is to brush the powder slightly over the surface with a soft camel-hair pencil; a very small quantity will adhere, and will communicate to the wax that metallic appearance so characteristic of plumbago. An exceedingly thin coating is attached; so thin indeed as scarcely to be visible, excepting by reflected light: this is sufficient for every purpose, and is even to be preferred to the thicker coating that may be given by several applications.

If a plaster cast is the subject of experiment, it will be necessary before black-leading it to destroy its absorbent property, otherwise, when put into the solution, it will absorb it, and the air which previously filled its pores will be expelled, and the mould will be covered with small bubbles, which obviously render it unfit for the reception of the metallic deposit. In order to prepare the plaster for experimenting in the electrotype apparatus, it is necessary to fill its pores by some substance insoluble in water, and capable of resisting the action of the cupreous solution. The various substances that will answer this purpose, are wax, tallow, spermaceti, linseed oil, and varnishes. As wax answers in every respect, and is superior to the other substances enumerated, we shall content ourselves with noticing its application. The wax should be well melted, and the plaster mould (which must be perfectly dry) should be immersed in it, and allowed to remain some minutes: it may then be removed, and placed, with its face upward, in a warm situation, until the liquid wax has disappeared from its surface; when it may be allowed to cool, and the black lead should be applied, as in the case of wax, with a soft brush.

The process of black-leading is equal to any process which has yet been made known. It is applicable to every substance likely to be used for the manufacture of moulds: wax, wood, plaster of Paris, sealing wax,* are equally susceptible of receiving a coating of this substance. Much difference of opinion has existed relative to the value of Mr. Murray's process: some have highly extolled it; while others have been loud in condemning it. These contradictory opinions are explained by the fact that there is a great difference between one specimen of black lead and another: one sample appears a perfect conductor, while another sample is an equally perfect non-conductor; and the only means of securing success in the choice of this article is actual experiment.

Our attention must next be directed to the precipitation of copper upon the mould or plate, prepared by any of the preceding methods. The manner of proceeding with the simple cell apparatus has been already described, and we shall now confine our attention to precipitation with the battery. The first step, after the preparation of the mould, is the attaching of a wire to it. If the mould is of fusible alloy, the wire may be readily attached by holding it for a few seconds in a candle, and melting it into the substance of the metal; or a hole may be made in the edge of the mould, and the wire being bent in the form of a hook, introduced in it, and thus suspended in the solution. If the mould or design is of wax, a wire should be melted into its edge, and the black-lead brush rubbed around the wire and the edge of the mould, so as to make a continuity of the black-leaded surface from the wire to the surface of the mould; if of plaster of Paris, the edge, as well as the surface of the mould, should be black-leaded, and a thin wire twisted round it; if the mould or plate is of lead, the wire should be soldered to its back. Whatever plan of attaching the wire is adopted, it is necessary to have a perfect connection between them. The wire thus secured to the mould, must be attached to the zinc of a single voltaic battery. The mould, immersed in a solution of sulphate of copper, to which a little sulphuric acid has been added, as hereafter fully explained, and a piece of waste copper to be dissolved, connected by a wire to the silver, copper, or platinum of the battery, must be placed opposite to the medal in the solution.

In the cases where a metal mould is used, it will be necessary to cover with wax, varnish, or some other non-conducting materials, those parts of the mould where the deposited metal is not required. This coating of the back and other parts requires to be done with care: if the smallest portions be exposed, they will receive a coating of copper, which is so much waste. Nor is this the only inconvenience—for, if the edge of the mould is left uncoated, the metal spreading on it will render the removal difficult, inasmuch as that part must first be cut away; and it will rarely happen that, under such circumstances, the mould escapes wholly uninjured.

* Sealing wax must be very slightly wetted with spirit of wine in order to receive the black lead. This substance should never be used where it may be avoided.

These precautions are of course unnecessary with moulds of wax and plaster of Paris; those substances, where uncovered with black lead, being non-conductors.

Immediately these conditions are complied with, the metal mould will be covered with a stratum of copper: if it be of wax, plaster of Paris, or any other black-leaded surface, this will not take place immediately; but the precipitated metal will be observed—first, to arrange itself round the conducting wire, and gradually to spread until it has covered the whole surface of the mould. The appearance of a mould on which the copper is spreading, is very beautiful: it goes on with a rapidity varying with the quality of the black lead; sometimes it will require an hour, or even a much longer time, to spread over the surface of a moderate sized medal; at other times it vegetates, as it were, with extreme rapidity, and its progress may be observed with the assistance of a lens, or even with the naked eye.

In placing a black-leaded surface in the electrotype apparatus, a very small plate, or even a wire, should at first be placed opposite to it as a positive pole. If this precaution be neglected, and a large plate at once introduced, the copper deposited near to the wire connecting the mould with the battery will be of very bad quality, owing to the want of that proportion between the quantity of electricity passing and the size of the negative surface, which is essential to the production of ductile copper. As more of the surface becomes covered, a larger positive surface may be exposed. This subject is treated on particularly a few pages hence.

After the surface of the mould is completely covered with the deposit, the operation will not require further attention, excepting, of course, renewing the acid of the battery. It is necessary to be very careful in observing, that no minute air bubbles are attached to the deep parts of the mould; these, of course, would spoil the deposited plate, as the copper cannot attach itself to those parts of the mould not in contact with the liquid. Sometimes the black lead (especially if a superfluous quantity be left in a deep part of the mould) will attach itself to one of these bubbles, and the copper spreading upon it, a perfect cast of the air bubble will be produced, and the operation rendered fruitless. These precautions having been observed, the experiment will proceed satisfactorily. If the surface on which the deposit takes place is small, a sufficient quantity of copper will accumulate in about six hours, supposing the apparatus to be in active operation. If the surface is a large one, such as a copper-plate, a much longer time must be allowed for the deposit to acquire additional thickness. It is only necessary to have a thickness sufficient to allow of the separation of the plate from the mould without risk of bending: any extra rigidity may be given more economically by the application of soft solder to the back, and by other means which will suggest themselves to every experimenter.

When small surfaces are exposed in the electrotype apparatus, it is

almost immaterial in what position they are placed; but when large surfaces are acted on, the position of the matrix or mould becomes highly important. If it is placed vertically, the deposited copper will possess various degrees of hardness from the different degrees of concentration of the upper and lower parts of the cupreous solution. We shall presently explain the laws by which the quality of the deposited copper is regulated; but we will anticipate that part of our subject by observing, that the metal may have an extreme hardness,—may be so crystalline as to break with the slightest touch, or be almost as soft as lead, and may assume every variety of texture between these extremes; and as these various characters are produced principally by the relation between the current of electricity and the concentration of the solution, the reader will appreciate the importance of attention to the position of the mould.

When the mould is vertical, the solution in contact with the bottom of it, losing a portion of its saline matter, becomes specifically lighter than the surrounding solution, and is, consequently, buoyed up; and as the same action is taking place at every part of the plate, an upward current is established on its surface; this current is of course greatest at the upper part, and it loses more and more of the cupreous salt as it approaches the top; this gives rise to a difference in the texture of the copper in different parts of the deposited plate.

Where a considerable thickness of copper is deposited in this way, the plate will exhibit a number of grooves on its surface, formed by this ascending current; the lighter liquid having found the most favourable channels, continues to flow therein, and, from the small amount of the salt contained in it, very little deposit accumulates there; while the intermediate portions being exposed to the more concentrated solution, the deposition goes on at those parts with facility; hence, the grooved appearance of the surface.

These inconveniences may in some degree be remedied by inclining the plate, so that the currents may rise through the liquid without passing over its surface; but with large plates, it is much more convenient to lay them in a horizontal position. In this case, it is necessary to place the mould or plate to be deposited on at the bottom of the vessel, and the copper-plate to be dissolved, over it; the precaution of introducing a piece of muslin or some such fabric between them must not be omitted, otherwise the impurities with which the copper to be dissolved is contaminated, will fall down as the pure metal is taken into the solution, and, lodging upon the mould, will at first impair its delicacy, and afterwards its solidity.

The reader may, perhaps, suppose that this objection would be obviated by reversing the position of the mould; that is, by placing it in the upper part of the vessel, face downwards, and the plate to be dissolved, under it. This plan is attended with so many inconveniences that it cannot be practised advantageously. There is, first, the

liability of minute portions of air being retained in the intricate parts of the mould, and from which, in its inverted position, it is scarcely possible to free it; and there is a still more weighty objection in the circumstance, that there is a greater irregularity in the state of the solution with this arrangement than with any other. The stratum in contact with the inverted mould, when deprived of a portion of its salt, being lighter than that immediately below it, has no tendency to give place to the more concentrated solution: when, however, this dilute stratum has accumulated a little, it escapes at the edges of the horizontal plate; and, by another portion becoming exposed to action, the process for a time continues to go on well. It is only, however, until the whole of the solution *above* the plate is thus deprived of its cupreous salt; there is then no tendency to circulation; the lighter fluid is in the upper part of the vessel, and the heavier at the bottom; the action becomes impeded, and the small quantity of copper deposited from such a dilute solution is of such a texture as to render it perfectly useless. The copper dissolved from the waste plate at the bottom of the vessel will crystallize there, while the upper part of the same solution is exceedingly dilute. These difficulties would not present themselves if a constant agitation of the liquid could be kept up; but this is obviously impracticable. The most convenient arrangement, then, is that in which the mould or plate to be deposited upon is at the bottom of the vessel, and the piece of waste copper to be dissolved above; in this case, as the solution is deprived of its salt of copper, it rises and gives place to a more concentrated portion, while the salt formed by the solution of the waste copper descends to the lower part of the vessel; and with such an arrangement the process goes on with much regularity.

The reader must particularly bear in mind that, in whatever position he may place the surface to receive the deposit, the piece of copper forming the positive pole must be parallel to it; if this condition is not observed, the deposit will be of different thicknesses at different parts; if the two surfaces are inclined to each other, a much greater thickness will be observed at the point where the two surfaces are nearest; and in proportion as they become more distant from each other will the thickness of the deposit diminish.

In precipitating copper upon very irregular surfaces it is difficult to obtain a deposit of uniform thickness; in such a case, it is desirable to bend the positive plate so as to assume the general figure of the negative surface; and when a sufficient thickness of copper has accumulated on those parts nearest the positive pole, the deposit may be removed from the solution, and they may be varnished or covered with some non-conducting substance, such as wax; on again introducing the surface thus treated, the copper will only be precipitated on the more distant or unvarnished parts; if the amount of surface thus defended from the solution is considerable, a difference in the texture of the copper will be produced, unless such alterations are made in the arrangement of the

apparatus as will be hereafter pointed out when treating of the conditions regulating the nature of the deposit.

Having now considered the circumstances to be attended to in the preparation of the surface to be deposited upon, and also the conditions to be observed in the arrangement of the decomposition cell, we will next proceed to enumerate the circumstances to be attended to in the preparation and management of the battery; and as the only modifications of that instrument likely to be used in electrotype processes are Daniell's, and the simple acid battery, consisting of a plate of zinc, and another of silver or copper, we shall confine our remarks to these instruments.

The first thing to be observed is the state of the zinc. If the amalgamation is perfect, there is not the slightest effervescence when plunged into dilute sulphuric acid; if there is any evolution of hydrogen from its surface, it must be amalgamated again. The plates of the acid battery may be plunged into a vessel containing one part of concentrated sulphuric acid to nine or ten parts of water; and if, by bringing one end of a clean wire against the binding screw connected with the zinc, and the other end in contact with the screw of the copper or silver, a violent effervescence arises at the latter metals, the battery is in perfect order. In preparing Daniell's battery, the porous cell should be filled with the dilute acid,* and the external copper vessel with a saturated solution of sulphate of copper, crystals of which salt should be placed on the perforated shelf in the upper part of the copper cylinder—care being taken that the surfaces to be brought in contact in making the necessary connections are perfectly clean—the instrument may be considered ready for use.

The reader must bear in mind that, in using a very dilute acid, a current small in quantity (and of an intensity dependent on the nature of the battery) will be generated, and that, by using a strong acid, a more copious current will be produced; he must also bear in mind that the strength of the acid employed does not in the least affect the intensity of the battery; a mixture of one part sulphuric acid, with a hundred parts of water, determines a current possessed of an intensity equal to that produced by acid of the strength recommended, though the latter gives rise to a much more copious current. For example, suppose a battery of a given number of plates, and charged with an extremely dilute acid, have its electrodes introduced into water, and that it does not possess sufficient intensity to decompose that water, no augmentation of the strength of that acid will enable it to do so. On the other hand, suppose the battery to have power to decompose water, and that it is charged with strong acid, the only effect produced by the most copious dilution will be a diminution of the quantity of water decomposed; but if the same number of pairs be preserved, however dilute the acid may be made, it will not lose its power to effect the decomposition.

* As before mentioned, a solution of sal-ammoniac or common salt may be employed instead of acid.

From the above remarks, the reader will perceive that the quantity of electricity generated in a battery may be regulated in two ways—either by altering the strength of the acid, or by exposing a greater or less extent of surface to its action. A small battery, charged with a strong acid, is the same in effect as a large one excited by weak acid, and *vice versâ*. The temperature of the apparatus has a very important influence on its action. If the battery and decomposition cell are heated artificially, the deposition goes on with much greater rapidity than under ordinary circumstances; on the other hand, in cold weather the process is very tedious, and if the temperature be extremely low it is completely arrested.

The solution in the decomposition cell may be a saturated solution of sulphate of copper, to which a little dilute sulphuric acid has been added. Two parts of saturated solution of the sulphate, and one part of dilute sulphuric acid (consisting of one-eighth concentrated acid) form a mixture which practice has shown to be equal, if not superior to every other.

Immediately the connections are made the deposition commences, and the mould or plate, if metallic, soon becomes covered with a thin coat of copper. After the apparatus has been at work a few minutes, it is advisable to examine the deposit, as its colour shows whether the process is going on properly or not. The appearance of electrotype copper is so characteristic that, when once seen, it can never be afterwards mistaken. If the arrangements of the apparatus are good, the metal will be tough and hard, and of a bright red colour, wholly unlike the copper reduced by ordinary processes; it may, perhaps, be more correctly described as of a pure orange colour; this, however, is only when the metal has the texture described. If the defective arrangement of the apparatus occasions a deposit of the brittle metal, its colour clearly indicates its character. Such metal has a dark, dull red appearance, wholly unlike the bright hue of the ductile metal.*

We will next proceed to treat of the various circumstances which interfere with the successful operations of the electro-metallurgist, and give rise, on

* A very interesting optical phenomenon may be observed, during the precipitation of copper in the electrotype. There are certain colours which, by mixture with other colours, produce white light; any two such are said to be complementary; thus red and green are complementary, because, white is the result of their mixture; blue and orange are also complementary, for the same reason. This formation of white light by the mixture of such colours, though exhibited in the utmost perfection in some of the phenomena of polarised light, is not often observed otherwise; owing principally to the rarity with which the colours are presented in a pure state. This phenomenon may however be observed in great perfection in the electrotype; the solution of sulphate of copper is of an intense and pure blue; and the newly-precipitated *ductile* copper is of an equally pure orange; let the reader take a vessel containing the cupreous solution, and place it in the sun in order to have an abundance of light, and immerse in it, in an horizontal position, a piece of new electrotype copper, a plate or medal in the course of formation, for example; immediately the metal sinks beneath the surface of the blue solution the orange tint fades, and, by placing it at a proper depth, altogether vanishes, and the metallic plate appears intensely white; when nicely adjusted, the plate so much resembles plaster of Paris, that a person unacquainted with the nature of the experiment, would with difficulty be persuaded that it was not made of that substance.

the one hand, to the deposition of the metal in a brittle or crystalline form, and on the other, occasion the appearance of the copper in the form of a black powder, having no cohesion.

The cause of the differences in the texture of the metal precipitated by voltaic agency is by no means well understood, though the conditions under which the various kinds appear are familiar to us. When a current of electricity of considerable intensity and large quantity is employed with a small negative plate, (the plate to be deposited upon) a black powder, wholly wanting in cohesion, is precipitated; if, on the other hand, a very feeble current be employed, with a large negative plate, an opposite effect will result—the precipitated metal will be crystalline, hard, and brittle. The circumstances which induce the former condition are too large or too highly-excited a battery,—a solution in the decomposition cell possessing too great a conducting power, produced by the addition of too much acid on the application of too high a temperature, or too large a positive plate of copper. The latter condition is induced by too small a battery, a neutral solution in the decomposition cell, a low temperature, or a large negative plate. The former defect, namely, the tendency to the precipitation of the metal in the form of a black powder, may be remedied by diluting the acid of the battery, or exposing a less surface of the metals to the strong acid; by diminishing the positive pole, or removing it to a greater distance from the negative.

The production of crystalline copper may be avoided by adding acid to the solution of sulphate of copper, by increasing the size of the battery, or by the application of heat. The medium between these extremes gives rise to the metal in the malleable or ductile form, the state in which it is usually required.

Mr. Smee refers the production of these states to the evolution of hydrogen in the case of the black powder, and the want of a tendency to its evolution in the case of a crystalline deposit; and when the arrangement is such that a small additional intensity or quantity would develope the black powder, the ductile metal is produced. As the evolution of hydrogen at the negative plate, or its absence there, depends entirely on the condition of the battery and decomposition cell, a reference to its production is only another way of expressing the condition of the apparatus.

The following table exhibits the results of a number of experiments, made for the purpose of exhibiting the effect of different relations between the size of the battery, the character of the solution, and the size of the electrodes. The battery employed consists of two plates of amalgamated zinc, between which is placed a plate of silver of the same size; the distance of the silver from each zinc is half an inch; the electrodes in every experiment were $1\frac{1}{2}$ inches distant from each other, and the average temperature 60° F.

BATTERY CHARGED WITH ONE PART OF CONCENTRATED ACID TO EIGHT OF WATER.

No.	Solution Employed.	Size of electrodes compared with each other.	Size of electrodes, (the largest where there is a difference) compared with negative metal of battery.	RESULTS.
1	Concentrated solution of sulphate of copper.	equal.	twice the size.	Distinct hard crystalline grains, dull red colour, very scanty.
2	Ditto.	positive half of negative.	equal.	Distinct hard crystals, red colour small in quantity.
3	Ditto.	equal.	equal.	Clusters of hard compact crystals, brilliant red colour, small quantity.
4	Ditto.	equal.	half the size.	Compact crystals so thickly clustered as to form a continuous stratum,—light red colour larger in quantity than above.
5	Ditto.			
6	Concentrated solution of sulphate of copper and one-twentieth of sulphuric acid.	equal.	twice the size.	Continuous stratum of fine crystalline structure, clay red colour having so little cohesion as to break on attempting to bend it.
7	Ditto.	positive half of negative.	equal.	Continuous stratum, brittle crystalline on surface, rather lighter colour than No. 6.
8	Ditto.	equal.	equal.	Continuous stratum, slightly ductile, fine crystalline surface, bright red colour.
9	Ditto.	equal.	half the size.	Continuous stratum, ductile, rather hard, very fine crystalline surface, bright red colour.
10	Ditto.	neg. half of positive.	equal.	Continuous stratum, ductile, rather hard, fine crystalline surface, red colour.
11	Concentrated solution of sulphate of copper with one-third diluted sulphuric acid.*	equal.	twice the size.	Continuous stratum, deficient in cohesion, crystalline surface, slightly ductile, rather hard, bright red colour.
12	Ditto.	positive half of negative.	equal.	Continuous stratum, ductile, fine crystalline surface, bright red colour.
13	Ditto.	equal.	equal.	Continuous stratum, ductile, rather hard, fine crystalline surface, bright red colour.
14	Ditto.	equal.	half the size.	Continuous stratum, not very ductile, very fine crystalline surface.
15	Ditto.	neg. half of positive.	equal.	Continuous stratum. ductile, rather hard, fine crystalline surface, large in quantity.

* Consisting of one part by measure of acid, and eight of water.

By an examination of this table, the reader will observe that, when the solution was neutral, and a large surface of electrodes exposed, the formation of distinct crystals was the result; that as the size of the electrodes was diminished, and their proportions made such as to determine a stronger current, the character of the deposit changed; and through the whole table he will trace a gradual improvement in the copper, as the circumstances which obstruct the passages of the current are removed. These circumstances, it is hardly necessary to remark, are the character of the solution, and the varying size of the electrodes.

The above table might have been continued to a much greater extent, but such extension would have been comparatively useless; the above shows what proportion must be avoided when the crystalline deposit is not wanted; and the reader will discover from it that, in order to obtain, with certainty, a good ductile metal, he must cause a more copious flow of electricity than is afforded by any of the arrangements there described, by increasing the size of the battery, or diminishing the size of the electrodes. The same effect will be produced by heat, A saturated solution, without acid, heated to 180° F., yields a tolerably good metal. The better way to effect it is, however, to use a larger battery. It will be found that, with the acidulated solution recommended, and an acid battery exposing twice the surface of the electrodes, (the latter being about $1\frac{1}{2}$ inches apart) the deposition will go on favourably.

The experimenter is strongly recommended to use, in his early experiments, a Daniell's battery in preference to every other. He is much less likely to fail in his operations by its use; and, from the extreme regularity of its action, the character of the deposit is not likely to change, even during a long experiment.

As a general rule, it may be remarked that there is greater danger of failure from a deficiency of power than from excess; the black deposit occasioned by the latter is at once apparent, but the brittle metal produced by the former may more easily escape observation.

We have hitherto spoken of the reduction of copper from the sulphate of that metal; though there are many other salts that may be used in the electrotype, and, as some of them possess advantages in particular cases, it will be necessary to examine these. The one claiming attention first is the *nitrate;* this salt is more expensive than the sulphate, but, as in the battery process, the only expense is the first solution, it may be very advantageously used. In the single cell apparatus it cannot be used, save at a great sacrifice of economy, as in that mode of operating, the solution requires the constant addition of the salt. The copper is deposited more rapidly from the solution of this salt than from any other. A pound of the nitrate may be dissolved in a pint and a half of water, slightly acidulated with nitric acid. The only other salt of copper deserving notice is the *acetate;* it may be prepared by adding verdigris, or oxide of copper to acetic acid, and crystallizing. Its only value consists

in its having no action upon iron, so that a die or surface of that metal may be immersed in a solution of this salt, and not receive a coating of copper, as is the case with the sulphate and most of the other salts of that metal. The experimenter will find this salt much less convenient for all other purposes than the sulphate and nitrate, and should only be used in cases where these salts are inadmissible. A compound battery of three or four cells must be employed for its decomposition.

The quantity of copper reduced by a given consumption of zinc is the same whatever salt of the former metal is employed. The equivalent of zinc is 32, and that of copper 34; consequently thirty-four parts of the latter will be reduced by the oxidation of thirty-two of the former.

Though not strictly connected with our subject, yet, as it may be interesting to those who pursue the art of Electro-Metallurgy for the production of fac similes of medals and objects for the cabinet, to be familiar with the processes by which a bronze appearance may be communicated to recently produced specimens, we will devote a few lines to the process that may be adapted to its production.

The simplest method of bronzing a production of the electrotype is to rub it with dry plumbago or black lead immediately, or within a few minutes after its removal from the apparatus, and, after heating it till it becomes too hot to touch, rubbing it briskly with a hard brush (a tooth brush answers well for small objects) until cold. On afterwards removing the superfluous black lead by a linen rag, the colour will be observed. With specimens that have been exposed some hours to the air this process is not successful. The operation of the plumbago in the production of the colour is not understood.

A bronze appearance may also be produced by covering the object with oxide of iron, and heating it in a muffle.

The application of hydrosulphate of ammonia to copper produces a sulphuret of that metal, which is of a beautiful colour.

A dilute solution of chloride of platinum, on being applied to brass and copper, stains them by the deposition of a minute portion of platinum in an extremely divided state, of a very beautiful colour; it is wholly unlike the bronze produced by age, but exceedingly beautiful. Objects thus bronzed should be handled very carefully, for it is easily rubbed off.

The voltaic precipitation of copper has been made available to many other purposes besides the multiplication of copper-plates, coins, and medals. Among other things, may be mentioned the production of plain copper-plates for engraving and etching, and the formation of vessels of different kinds. Plates for engraving may be made by depositing the metal upon a burnished piece of copper. In this case, the precipitated plate will have a burnished surface like the copper on which it is deposited; or it may be precipitated on a plate not so prepared, and be afterwards treated exactly as ordinary copper is for the use of the engraver. The arrangement of the apparatus necessary for the production of a copper

of a proper quality has been so fully pointed out that it is unnecessary to repeat it here. Copper-plates intended for etching, when made by the electrotype process, are so superior to those of ordinary copper, that there can be no doubt the former will very soon completely supersede the latter. The electrotype metal is absolutely pure, and hence, in all chemical processes, is more uniformly acted upon than any other. The electrotype itself will demonstrate this. The copper forming the positive pole in the decomposition cell invariably presents a black surface during its solution, and a quantity, more or less, of scaly matter, consisting of charcoal and other impurities, is invariably left behind where thick plates are thus operated upon; but, if a piece of electrotype copper is used as a positive pole, its surface does not for a moment lose the beautiful orange colour so peculiar to it; and, after the largest masses have been dissolved, not a particle of impurity is left behind—nay, the beautiful transparency of the liquid is not in the slightest degree impaired. Hence it is that, in the process of etching, the common or impure metal proves a source of anxiety, and often disappointment to the engraver, while he uses that precipitated by voltaic agency with the absolute certainty of success. When the acid is applied to the former, its action is frequently intense in one place and feeble in another, and the etching is of necessity irregular; but with the latter the utmost uniformity of action prevails, and a corresponding regularity in the product results. From what has been said of the action of impurities in zinc, when treating of the voltaic battery, the reader will at once understand that the impurities may in some instances accelerate, and in others retard the action of the acid, according to their nature.

A very ingenious application of the electrotype has been made by Mr. Palmer, and called by him "electrotint." It consists of a kind of painting, executed upon a stratum of semi-fluid composition, spread on a metallic plate: the surface of the composition is made a conductor of electricity; and a deposit of copper being made upon it, a metallic surface is produced, exhibiting the design originally drawn upon the composition, and capable of being printed from. By this process two kinds of plates can be produced: the design may be prominent, as in the case of a wood engraving, and the impression obtained from the surface of the design; or, it may be sunk beneath the surface of the plate, and the impression obtained as from ordinary copper-plates: the latter promises to be the more useful. We will describe the processes in detail.

To produce a plate to be printed from as an ordinary copper-plate, a stratum of a composition consisting of one part of wax, two of lard, and one of lamp-black, is spread upon a plate of German silver, plated copper, or some other white metal, either polished, or having a "dead white" surface; to which has been previously soldered a wire, to connect it with a voltaic apparatus. Now, if a number of lines were drawn through this composition, so as to expose the white plate, and the whole surface made a

conductor of electricity by black lead being spread upon it, a plate of copper can be produced from it in which the lines drawn in the composition will project. If such a plate be printed from by a copper-plate printer, the impression produced will exhibit the projecting parts white, and the depressed ones black. In the mould, the lines drawn were white, for the surface of the white metal was exposed, and the untouched parts were black, being the black composition; hence, in order to produce a design, it is only necessary to remove the black composition, so as to expose the white plate where whiteness is wanted in the printed impression, and where blackness is desirable, to leave the black composition; where intermediate shades are required, the composition may be partially removed, so that the white plate appearing through the thin stratum of the composition, gives the desired tint. To produce the effect of a picture, the artist takes the plate prepared as above, and by means of brushes of various degrees of hardness, removes the composition in such a manner that the white plate appearing more or less through different parts of it, gives the effect he desires to produce. Different styles of handling may be adopted: by means of soft brushes, the smoothest tint may be produced; and by harder tools, a coarser or bolder effect may be obtained. As the composition never sets or becomes hard, any defect may be remedied by spreading the composition over it, and working it again. Although the principle on which these paintings are produced is very simple, they are by no means easy of execution; for, although the effect wished may appear on the prepared plate, the impression produced from the copper-plate may have a very different appearance; for it is not only on the depth which may be given to different parts of the composition, but on the *character* of the surface that the depth of colour depends. Where perfect blackness, for example, is required, it is not enough that the composition be left unremoved—that will give the effect in the plate drawn on, and the electrotype plate produced from it will exhibit a depression in that part—but when it is printed from, the ink will be removed by the printer's hand, and the part will print white. In such cases, it is indispensible to produce, by means of different tools, such a texture of surface that the ink shall be retained thereon.

The other kind of plate produced by this process, viz., that from the surface of which the design is to be printed, is produced by a process similar to the foregoing; the principal difference is in the preparation of the plate, which is in this case black, and covered with a white composition. The reason for this difference is obvious. In the former kind of printing, the projections were left white, and the depressions gave the dark tints, in the present case, the projecting parts gave black, and the depressions white; hence, it is necessary to have a black plate covered with a white composition, by removing which the black plate becomes exposed and form the dark parts of the design; where white parts are required, the white composition is left. A copper-plate

may be blackened by being washed with a solution of hydro-sulphuret of ammonia or chloride of platinum; and the white composition may be either a mixture of two parts of sulphate of lead, two of lard, and one of wax; or sulphate of lead and olive oil mixed in such proportions as will give a proper consistence. The drawing may be executed with various tools so as to produce various effects; but it is unnecessary to go into detail on the subject, as the work can only be executed by an artist,—and he is quite familiar with the nature of the tools to be employed, to produce the result he requires. After the drawing is made, the finest black lead is sifted on to its surface, and any superfluities removed by an exceedingly soft and dry camel-hair brush; and it is exposed in the electrotype apparatus in the manner pointed out for the copying of copper-plates.

Having thus treated of the precipitation of metals at the negative pole of a voltaic battery, and explained the various conditions necessary to the successful practice of the arts which have resulted therefrom; we will next direct attention to the important art to which the solution of metal, at the positive pole of such an apparatus, has been made subservient—namely, voltaic etching.

The process by which etching on copper is ordinarily effected is so generally known, that we shall only very briefly allude to it. The plate is covered with a thin layer of what is technically called "ground;" it is a composition the principal ingredients of which are wax and pitch. It is applied by being rubbed over the copper-plate while heated. By means of a pointed instrument, the artist traces the design he wishes to etch; the composition is removed wherever he has drawn, and the surface of the copper consequently exposed; the plate is placed in a vessel, and dilute nitric acid poured on it; the copper is dissolved wherever the acid comes in contact with it; and the lines drawn thus become permanently etched upon the plate. It is necessary to examine the work as it progresses, and to remove it from time to time, to "stop out" those parts where the lines are not required to be deep: this process consists in covering such parts with varnish or composition, which will defend them from the further action of the acid. This part of the work requires considerable attention, as much of the beauty and perfection of the result depends upon it. Notwithstanding the diligence and care of the workman in the production of the design and the surprising address with which he "stops out," from time to time, those parts which have been sufficiently acted on by the acid, the operation is often more or less unsuccessful.

When treating of the purity of the electrotype copper, we took occasion to notice the cause of the irregular action of the acid upon the metal reduced in the ordinary manner, and the superiority of that produced by voltaic agency. We are now about to describe a process by which the etching itself may be accomplished with far more ease than by the common method, and with a certainty of success unattainable by any other mode of procedure.

From the various experiments which have been already described, the reader is familiar with the corrosion or decay of the copper, of which the positive pole of a voltaic arrangement is made; and he is also familiar with the fact, that if the negative plate in a voltaic arrangement be covered with a varnish, or some non-conducting substance, all action will be suspended at that part: accordingly, wherever a deposit of metal was not wanted in any of the experiments before described, we have directed such parts to be thus treated. Precisely the same holds good with respect to the positive surface; only that part of it is acted upon which is in actual contact with the liquid, and the slightest film of any foreign substance effectually defends it from corrosion. It is upon these facts that the art of Voltaic Etching is founded.

The plate to be etched by the voltaic battery is prepared in the usual way, both with regard to the laying of the ground and the tracing of the design; it is then carefully varnished on the back and edges, and a wire is attached to some part where the copper is exposed: this latter must be done very carefully, as it is desirable to varnish it over afterwards. The wire is connected with the copper, silver, or platinum of a single voltaic battery, and a plate of copper of the same size, connected with the zinc, is placed in the solution, opposite to, and parallel with, the plate to be etched. The deposition of copper immediately commences upon the negative pole, and the lines, or other exposed parts of the positive plate, yield up metal to the solution. It is evident, that it is immaterial whether the deposit on the negative plate is in the form of ductile metal or not, and the various circumstances with regard to the battery, which have been pointed out as essential to its production, need not in the present case be regarded; as the attention should be wholly directed to the conditions requisite to secure the uniform etching of the plate. The battery may be a single pair, as above stated, or a series of two or three may be employed; with the former the action will be slower than with the latter. The distance of the two plates in the solution will also materially affect the rapidity of the process; by placing them near each other, a more rapid action will be induced, and by removing them to a greater distance, a corresponding retardation will follow. The copper-plate serving as the positive pole should be as near the size of the surface to be etched upon as may be: if it is larger, the lines near the edge of the plate will be more acted upon than those nearer the centre; and, on the contrary, if it is smaller, the centre will be more deeply etched than the edges. In some cases, however, such an effect is desirable, and it can be produced by the voltaic process far more accurately than by the ordinary method. A greater or less depth of the lines is effected in the common process, by stopping out portions from time to time—that is, covering with a varnish those parts which have been sufficiently acted upon by the acid, so as to defend them from farther action.

This mode of operating, however, does not enable us to effect a gradual

transition from faint to deep lines; it is only by the voltaic process that this beautiful effect can be produced. If a plate be prepared, having a series of parallel lines drawn upon it, and be submitted to the action of the battery in the way already described, the lines will be etched with perfect regularity of depth if the negative plate be parallel to it; but if they be inclined to each other, the lines will be made deep at that end where they are nearest, and will be faint at the end where they are most distant; an impression from such a plate will exhibit at one end a very dark tint, which, gradually fading, will leave the other end very nearly white. It is obvious, that this effect may be varied to a very great extent; if, for example, a prepared plate, having lines of uniform width ruled upon it, be experimented upon, and the negative pole in the decomposition cell be a circular disc, placed opposite to the centre of the plate, the lines will be deepest in the centre and fainter at the edges, and a surface printed from such a plate will exhibit a dark spot, the edges of which melt imperceptibly into the surrounding light: or the reverse effect may be produced, if the negative be made of the size of the positive plate, or that to be etched, and have a circular hole made in its centre; the lines on the middle of the etched plate will be very faint and those near the edge very deep: an impression taken from such a plate has a dark ground with a luminous spot in its centre, the light of which becomes gradually fainter from the centre, and is eventually lost in the surrounding darkness. The effects now described may be modified in several ways; indeed, there is no limit to the varied effects of light and shade which may be thus produced; and it is scarcely too much to assert, that the most beautiful designs may be produced by this mode of treatment, upon a plate on which parallel lines only have been drawn; for, by using a positive plate of the size of the negative or prepared plate, and perforating it in different forms, the etching will go on rapidly where the metal is presented to it; and the parts where no metal is opposed will be left more or less unacted upon; hence a proof from the plate will have a dark ground, and this design cut out of the negative plate will be left light. Or, if preferred, dark designs upon a light ground may as easily be produced; for if, instead of cutting out the pattern, the negative plate be cut into the desired form, the design will be deeply etched, and the impression will give a dark figure upon a light ground. Where it is desired to give very slight gradations of shade, or to produce in this manner complex figures, the better way of operating is, to make the surface of the negative plate to project in those parts opposite to which deep etching is required, and to be more distant where light is required. In other words, the negative plate should be embossed; and as it need not be thick there is no difficulty in giving it the proper figure; the parts most prominent will give shadow, and those most depressed will leave light, and, as the projections and depressions are more or less abrupt, will the transition from light to darkness be more or less gradual. It is very important, however, for the experimenter to remem-

ber, that the distance between the plates affects the result in a very important manner; the closer they are the more accurately will the design on the negative be etched on the positive plate, and as they are gradually placed farther apart will the figure on the former become indistinct on the latter; indeed, a plate, however embossed or cut away, will leave little or no trace of its figure on the positive surface, if it be placed very distant from it in the solution. The cause of this is sufficiently evident; when the embossed surface is very near to the plain one, the distances of the raised and depressed parts from the plain surface are very disproportionate; but when placed at a distance, the disproportion becomes less, and at great distances altogether insignificant. Now, if we suppose the action to be inversely as the distance, the effect of placing the plates near to each other will be to render the disproportion between the distances of the different parts of the embossed plate from the plain one, very great; and the difference in the amount of action on the opposed surface proportionably great; by placing them more distant, this difference vanishes, and with it the difference of action. It is evident that the same applies to perforated plates, or those cut in peculiar form, and also to plain plates inclined to each other.

The advantages which the voltaic process of etching possesses over the ordinary one, are,—its certainty of success,—the absence of gaseous matter on the surface of the plate, which in some degree interferes with the action of the acid,—and the clearness of the lines produced. We may also add, that the rapidity of the process can be regulated at the will of the operator,—that the progress of the etching may be at any time examined without inconvenience,—and that, besides permitting the regulation of the action by the process of stopping out parts of the plate, it affords a means of effecting gradations of shade wholly unattainable by any other known method of etching.

The most beautiful application of the voltaic process of etching is that made by Mr. Grove. This gentleman has succeeded in etching, by the voltaic battery, those beautiful pictures formed by the process of M. Daguerre. It is necessary to allude to the process by which these pictures are formed, in order that the subsequent process of etching may be intelligible. A plate of silver, or of copper plated with pure silver, is carefully cleaned by the action of pounce, or pumice powder, and acid, and is afterwards exposed to the vapour of iodine, until, by the condensation of that element upon the silver plate, a gold colour is produced. The plate thus prepared, is extremely sensitive to light; it is introduced into a camera obscura, so as to receive upon its surface the images of objects to which the camera is directed, and which are formed in the focus of its lens. The plate is allowed to remain under the influence of the light, for a time, varying with the season of the year, the clearness and brightness of the day, &c. Upon removal, it is exposed, in a close chamber, to the vapour of heated mercury, by which operation, the images of the objects thrown upon it

while in the camera obscura, become developed; the mercury attaches itself to those parts where the light had fallen, and forms an amalgam, which has a crystalline texture, and a dead-white appearance. The plate is washed with a solution of common salt or a solution of hyposulphite of soda; which process removes the iodine, and the plate is no longer sensitive to light.

On examining a daguerreotype plate, it is necessary to hold it in such a position that the incident light, (the light by which it is illuminated,) shall not be reflected from its whole surface to the eye; otherwise the objects will not be visible, and the plate will only present a uniform brilliant surface; but, by the spectator placing himself in such a position, with regard to the plate, that the light falling on it is reflected in another direction, the picture immediately becomes visible. The light parts in the objects consist of an amalgam of mercury and silver, the crystalline surface of the amalgam scatters the light in different directions; and a portion of it consequently reaches the eye; hence, the whiteness of those parts: and the dark portions of the picture are those places where the mercury has not attacked the silver, and the light falling there is regularly reflected from the brilliant surface of that metal, and none of it reaching the eye, it presents that black appearance so peculiar to highly-polished metallic bodies. The intermediate lights and shades, are where the texture of the surface is more or less altered, by the action of a greater or less quantity of mercury.

The chemical constitution of such a plate is therefore as different in different parts as is its physical structure, and it is by availing himself of this fact that Mr. Grove has effected the etching of these beautiful productions. The daguerreotype plate is varnished on the back and sides and connected with the platinum of one cell of Mr. Grove's battery, and to the zinc is attached a plate of platinum on which the fine powder of platinum has been deposited; such a surface parts with the hydrogen liberated upon it very freely. The two plates of an equal size are placed in a vessel containing a mixture of two parts of hydrochloric (muriatic) acid, and one of water; the plates are placed at the distance of about one-fifth of an inch, and, by being made to slide in a grooved wooden frame, are maintained perfectly parallel, and at the proper distance from each other. In about thirty seconds the best effect is produced; if the operation be continued much longer, the beauty of the picture will be impaired; the etching will be deeper, but some of the fine lines running into each other, the exquisite minuteness of detail for which these pictures are remarkable, will be destroyed. The plate on removal from the solution, is washed in distilled water, and the brown deposit formed upon it removed by a dilute solution of ammonia; for this purpose it is placed in a shallow vessel containing the solution, and gently rubbed by soft cotton. A second washing and drying completes the process. These plates are not etched to sufficient depth to enable a printer to take good impressions from them, as the ink is not

well retained in the deep parts, and the beauty of the plate is destroyed by the process of cleaning it.

Daguerreotype plates may be copied in copper by the electrotype; some of them, however, are very faint, and a repetition of the process more or less injures the original, but the most beautiful impressions may be taken from plates operated upon in the manner described, and an almost unlimited number may thus be procured, without injuring the original.

The precipitation of the noble metals received early attention at the hands of those who experimented with the electrotype, but the successful application of the voltaic battery in their reduction is of but recent date. Mr. Spencer relates experiments he made with gold, and describes a plan of effecting its reduction, which, (though the materials are in connection with the voltaic battery) is wholly unconnected with electric agency. The plan alluded to consists in forming an arrangement similar to that of the single cell apparatus represented in *fig.* 8. The porous cell is charged as usual, and the outer vessel filled with a very dilute solution of the chloride of gold, to which a few crystals of carbonate soda have been added. If a battery and decomposing cell be used, Mr. S. recommends that the former be charged with cold water only. A film of gold is deposited on the surface thus treated, but it is extremely thin; and, however long the connection with the battery is maintained, it cannot be made thicker—a sufficient proof that the cause of the deposition does not exist in the battery; indeed, the effect is produced without the battery, and therefore cannot with any propriety be called a voltaic precipitation. A mode of precipitating gold has been described in the "Annales de Chimie," by M. de la Rive. It is essentially the same as that of Mr. Spencer. The process is described at great length by M. de la Rive, but, as it is so inferior to the methods at present adopted, it is useless to describe it. Subsequent experiments have supplied us with processes by which works of art may be multiplied in gold and silver with as much ease as in copper.

Platinum may be precipitated from its chloride, gold from its combination with chlorine, iodine,* bromine, and cyanogen,* or from its oxide dissolved in potassa or soda, and silver may be produced from its cyanide,* acetate, sulphate, or the solution of most of its salts in ammonia. The chloride of platinum is made by the addition of spongy platinum, or the ordinary metal in small pieces, to nitro-muriatic acid or aqua regia; the latter is composed of one part of concentrated nitric acid, and two parts of muriatic (hydrochloric) acid. Chlorine is liberated, and is the real solvent. The chloride of gold may be prepared in the same way, and from the concentrated solution, oxide of gold may be precipitated by the addition of caustic potass. The bromide of gold is formed by the simple

* * * The reader must bear in mind that the use of these salts for plating or coating metallic bodies with a film of gold or silver has been patented.

addition of gold to bromine. The cyanide of gold is easily procured, by dissolving either metallic gold, or the oxide of that metal, in a solution of cyanide of potassium. If metallic gold be used, it must be in a state of minute division, and its solution may be promoted by the application of heat; it is, however, a very tedious operation. The oxide dissolves very readily. Two ounces of the cyanide of potassium may be dissolved in a pint of water, and the oxide of gold added till the solution will take up no more. The cyanide of potassium may be made in various ways. It may be formed by the direct union of its elements; if potassium be heated in cyanogen it burns with a beautiful flame; cyanogen is absorbed, and the cyanide of potassium formed. This process cannot be used for its production in large quantities. The simplest and most economical mode of forming it is to heat the salt known by the names of prussiate of potass, ferroprussiate of potass, and ferrocyanide of potassium. It is known in commerce as prussiate of potash. It should be put in a close vessel, and heated to redness, and, after cooling, the addition of water will dissolve away the cyanide of potassium, which may be obtained in crystals by the ordinary process. The latter, however, is not necessary, as it must be used in the state of solution. The compounds from which silver can be reduced are thus prepared. The cyanide, by the addition of oxide of silver to the solution of cyanide of potassium, the acetate by adding oxide of silver to acetic acid, or a solution of acetate of potassa to the solution of nitrate of silver. Sulphate of silver may be procured by boiling silver in sulphuric acid, or adding sulphate of soda to nitrate of silver, and the carbonate is precipitated when carbonate of potassa is added to a solution of nitrate of silver. The latter is prepared by dissolving silver in nitric acid, diluted with an equal quantity of water. The oxide of silver is prepared from this solution by adding a solution of caustic potass, or soda, or lime water. An olive coloured precipitate falls, which is the oxide. The carbonate of silver and most of the other salts of that metal, which are insoluble in water, dissolve very readily in a solution of ammonia, the metal may be reduced from such solutions; but they possess no advantages; and the fact, that the detonating compound called fulminating silver is produced by the solution of the salts of silver in ammonia, is sufficient to induce the experimenter to reject them.

The nature of the moulds or surfaces on which the deposit is to take place requires attention. There are very few of the salts of gold and silver which do not suffer decomposition by contact with other metals. Thus, if a piece of copper, brass, &c., be immersed in a solution of any of these salts, a precipitation occurs upon it, sometimes in the form of a perfect layer of silver or gold, and at others in the form of a dark powder. In using such metals it is advisable to make all the connections with the battery before introducing the surface on which the deposit is to take place into the solution. When such a course is adopted, the mould or surface receives a thin film of gold by voltaic action, immediately on being intro-

duced, and there is very little action upon it. If this precaution be not taken, the precipitation alluded to will take place, and the surface to receive the deposit will be injured; as much metal will be dissolved from it, as is equivalent to that deposited upon it. Although the whole of the salts of gold before mentioned may be reduced for the reduction of that metal upon a surface of gold, and those of silver upon a silver surface, yet, with every precaution, many of them are wholly unfitted for reduction upon baser metals, such, for example, as copper, brass, or iron. Those least objectionable are the cyanide of gold, and the solution of its oxide in potassa or soda, and the cyanide of silver and its ammoniacal solutions. The cyanide of silver possesses no action on iron, and may be therefore advantageously used for its reduction upon that metal.

To precipitate platinum in a bright continuous film, a weak solution of its chloride should be employed, with a battery charged with very dilute acid. The positive pole should be exceedingly small—a fine wire for example.

When it is desired to precipitate platinum in the form of a black powder, as in the platinized silver used in Smee's battery, an acid solution of the chloride should be employed with a copious current of electricity. An arrangement similar to a single cell of Grove's battery is very convenient for this purpose. (See *fig.* 7.) The plate of silver on which the platinum is to be precipitated is placed in the porous cell, together with dilute sulphuric acid, containing a small quantity of the chloride of platinum. On touching the silver against the zinc, an effervescence occurs on the former by the escape of hydrogen, and the black powder is thrown down.

It is necessary to take precautions to avoid the adhesion of the precipitated metal to that on which it is deposited, when such a result is not wanted, or to secure it where desirable. There is much less risk of adhesion between dissimilar metals than there is when the mould receiving the deposit is of the same metal as the deposit itself; and in the former case it is very difficult to effect an adhesion—in the latter to prevent it. When the experimenter wishes the deposit to adhere, he must thoroughly clean the surface to which it is to attach itself. This may be effected in a variety of ways, but there is none so effectual as its immersion in acid; and there are few cases in which the article can be injured thereby, for the metal to be deposited upon it must effectually hide the slight change produced in its surface where there is any action upon it. Dilute sulphuric acid may be employed, or dilute nitric acid; the latter attacks most metals—the former very few. The action of nitric acid is very effectual, for the roughness of surface which it leaves is very favourable to the adhesion of the deposit, and, where admissible, the roughening or scratching of the surface by mechanical means may be resorted to. The process called by workmen "dipping," prepares a

surface admirably for the reception of the precipitated metal, where its adhesion is desired.

When the precipitated gold or silver is to be removed from the surface on which it is deposited, the latter should be carefully protected from the treatment last recommended; and if it has been found necessary to heat it or immerse it in acid, it should be allowed to remain exposed to the air, in a cold situation, many hours, when the effect produced by such treatment will be counteracted. A piece of metal, when dipped in water, does not generally become wetted; and if metal in such a state be deposited upon it by voltaic agency, it generally does not adhere; on the other hand, if it be heated, or a fresh surface be exposed, either by mechanical means, or by immersion in an acid, which acts chemically upon it, water will attach itself to it, and in such a case it is favourable to the adhesion of the deposit.

The reduction of the noble metals may be effected either by the single cell apparatus or the battery: the latter is unquestionably the better, both for convenience of management and for its economy. The former may be modified in the various ways represented when treating of the reduction of copper where small articles are to be deposited upon. The best form of the apparatus, is that represented in *fig.* 8, excepting that the interior or porous cell should receive the solution from which the metal is to be reduced, and the external vessel should contain the zinc. The remarks made on the relations to be observed in the various parts of the apparatus for the reduction of copper, apply to the reduction of the noble metals, indeed the extremes between which gold and silver are deposited in a proper form, are much more limited than in the case of copper.

The reader must bear in mind that the equivalent numbers of these metals are much higher than that of copper: the equivalent of gold is 200, and that of silver 108; hence 200 grains of the former and 108 of the latter will be reduced to the consumption of 32 of zinc. These metals will, consequently, be deposited much faster than copper, and hence a much smaller amount of electricity should be employed. The surface of zinc may be reduced, the acid may be more dilute, or the positive pole much smaller in size. The cyanide solution is on the whole the most convenient from which to reduce gold or silver.

The character of the deposit of gold or silver is influenced by the state of the current employed, as in the case of copper, and the remarks made on this subject, when treating of the reduction of copper, are applicable in general to the reduction of other metals. There are, however, two or three circumstances in relation to this subject, which require especial attention. The solution of cyanide of silver cannot have its conducting power increased by the addition of sulphuric acid, as decomposition of the salt would take place; hence, the only means we have of regulating the flow of electricity are the quantity of the cyanide in the solution, its temperature, and the intensity of the battery. The solution of two ounces of the cyanide to a pint of water, and saturated with oxide of silver, answers exceedingly

well, and, as the maintenance of an elevated temperature is very inconvenient, it is necessary to use a battery possessing considerable intensity: three or four cells of the acid battery will answer the purpose; but a Daniell's battery is far more convenient, and cannot be too strongly recommended for the purpose in question. When the arrangements are properly made, the deposited silver is of a beautiful whiteness, and tolerably smooth on its surface. If the flow of electricity be too great, the silver is of a dirty yellow or brown colour. The remedy is so obvious from what has been already said, that it is unnecessary to do more than thus allude to it.

THE END.

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ERRATUM.

In page 6, line 30, for "oxide of potassium," read "iodide of potassium."

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